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## Synthesis and Crystal Structure of Guanidinium L-Monohydrogentartrate: Encapsulation of an Optically Nonlinear Octupolar Cation

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### Abstract

Encapsulation of an optically nonlinear octupolar guanidinium cation in a host polyanionic L-monohydrogentartrate lattice leads to a noncentrosymmetric orthorhombic  $P2_12_12_1$  guest–host crystalline structure with cell parameters  $a = 11.347$  (2),  $b = 11.162$  (2),  $c = 6.668$  (2) Å with  $Z = 4$ . Final  $R = 0.049$  from 1229 independent reflections. The packing shows strong interlocking between the anionic and cationic sublattices by a multidirectional hydrogen-bonding network. The optimally oriented octupolar crystalline structure for the 222 crystal point group is defined and the corresponding reference maximal nonlinear susceptibility is compared to that of the present guanidinium crystal structure thus pointing out possible improvements *via* appropriate structural modifications.

### Introduction

The engineering of guanidinium L-monohydrogentartrate  $[\text{C}(\text{NH}_2)_3^+ \cdot \text{C}_4\text{H}_5\text{O}_6^-]$  single crystals follows a new direction in the conception of quadratic nonlinear optical materials. Over the last ten years organic materials made up of molecules containing polarizable  $\pi$ -electron systems asymetrized by inter-

acting electron donor and acceptor groups have been extensively developed. Nitroaniline derivatives (Nicoud & Twieg, 1987; Oudar & Hierle, 1977; Zyss, Chemla & Nicoud, 1981; Zyss, Nicoud & Coquillay, 1984), stilbenes (Wang, Tam, Stevenson, Clement & Calabrese, 1988; Tam, Guerin, Calabrese & Stevenson, 1989), cyanobiphenyls (Zyss, Ledoux, Bertault & Toupet, 1991), push–pull polyenes (Barzoukas, Blanchard-Desce, Josse, Lehn & Zyss, 1989) and polyphenyls (Ledoux, Zyss, Jutand & Amatore, 1991) are noteworthy molecules for quadratic nonlinear optical applications. The variety of chemical substitutions provided by organic chemistry guided by empirical as well as more elaborate theoretical models has allowed for the targeted tailoring of optimized crystals towards quadratic nonlinear optics (Zyss & Oudar, 1982; Zyss & Chemla, 1987). Molecular nonlinear evaluations from the EFISH experiment (Levine & Bethea, 1974; Oudar & Le Person, 1975, 1976; Ledoux & Zyss, 1982), related by an oriented gas model, have been very useful for selective development of such crystals. Besides purely crystallographic structural considerations, the spectral adequacy of crystals has also been discussed, in view of applications, in terms of a 'transparency-efficiency' trade-off based on both molecular (Zyss, 1991a) and excitonic considerations (Zyss, Ledoux,

Bertault & Toupet, 1991; Pierre, Baldeck, Block, Georges, Trommsdorf & Zyss, 1991). These advantages of organic molecules, in contrast with minerals where similarly clear molecular-engineering rules are not available, have permitted the exploration of useful directions for synthesis. However, there remains room for suitable chemical variations, even in the apparently clear-cut case whereby chirality forbids, in principle, a centrosymmetric structure: the arrangement of possibly optimized molecular units in acentric packings may not depart sufficiently from centrosymmetry (Ziolo, Gunter, Meredith, Williams & Troup, 1982), hence resulting in low macroscopic susceptibilities. The challenge for chemists is to find original acentric packings optimizing phase-matchable nonlinear coefficients while maintaining a broad transparency range. Additional features such as a high pulsed and continuous-wave optical-damage threshold and a potential for crystal growth of large-size high-optical-quality samples are also of crucial importance. To reach an optimized acentric structure such as that exemplified by *N*-(4-nitrophenyl)-L-prolinol (NPP) (Zyss, Nicoud & Coquillay, 1984), various crystal-engineering strategies have been explored. Over the last few years, attempts towards the encapsulation of organic molecules in inorganic subnetworks resembling molecular sieves have been undertaken (Cox, Gier, Stucky & Bierlein, 1988), while association of stilbene derivatives with various organic and inorganic anions has been demonstrated by Meredith (1983).

The encapsulation of highly polarizable organic molecules of ionic character between chains or layers of inorganic or organic polycondensed anions is a worthwhile approach for building anisotropic and acentric crystalline frameworks capable of anchoring well ordered organic entities. Moreover, organic salts that are built up through short hydrogen bonds are often less sensitive than molecular compounds to external chemical agents and offer mechanical and thermal properties approaching those of minerals. Use of the  $(\text{H}_2\text{PO}_4^-)_n$  flexible polyanion in the crystal engineering of layered polar materials has recently been studied (Aekeroy, Hitchcock, Moyle & Seddon, 1989; Masse & Durif, 1990) and is exemplified by the 2-amino-5-nitropyridinium dihydrogenmonophosphate crystal (Masse & Zyss, 1991), which exhibits interesting nonlinear-optically efficient properties (Kotler, Hierle, Josse, Zyss & Masse, 1992). In the present case, the synthesis of guanidinium L-monohydrogentartrate is an approach aiming at the encapsulation of guanidinium cations between helical chains formed by the aggregation of L-monohydrogentartrate anions with the potential to organize the corresponding cations in an acentric layered or one-dimensional framework. Previous research in the domains of molecular and crystalline

engineering towards the enhancement of quadratic nonlinear-optical properties had almost exclusively focused on asymmetric intramolecular charge-transfer conjugated molecules, with *p*-nitroanilines as prototype systems. Such molecules tend to sustain large dipole moments in the ground state and exhibit an elongated dimension parallel to their main charge-transfer axis  $\mathbf{u}$ . Furthermore, the anisotropy of the polarizable  $\pi$ -electron system will be reflected in the reduction, to a good approximation, of the quadratic hyperpolarizability  $\beta_{ijk}$  tensor to a single non-negligible  $\beta_{uuu}$  coefficient. Various problems linked to the anisotropy and anisotropy of such dipolar systems have been pointed out (Zyss, 1991*a*).

(i) Isotropic spheroidal objects tend to pack more readily in an ordered crystalline lattice than elongated and rod-like objects. The ease of crystal growth is thus expected to benefit from a better packing geometry based on a molecular design favouring higher symmetry together with a more rounded shape.

(ii) Large dipole moments, which are often associated with the potentially detrimental elongated shape of traditional nonlinear candidate molecules, are not a prerequisite to the existence of quadratic nonlinear properties: nondipolar molecules corresponding to trigonal, orthorhombic and cubic point groups, among others, are noncentrosymmetric and able to sustain a nonzero and possibly optimized  $\beta$  tensor, as recently outlined by Zyss (1991*b*).

A complete description of such groups denoted as 'octupolar' point groups whereby all observable quantities of dipolar symmetry strictly vanish is given by Zyss (1992). Expressions for the associated  $\beta$  tensors and an intrinsic character-table-based identification procedure for multipolar groups are also detailed. It is shown in particular that different tensor coefficients can be optimized, leading to practical advantages such as pertain to the electro-optic Pockels effect and related applications, in contrast to the traditional case where one dominant component is singled out.

As an example, a general expression for the  $\beta$  tensor of a planar  $D_{3h}$  molecule with the axis convention shown in Fig. 1 is

$$\beta = \beta_0(\mathbf{y} \otimes \mathbf{y} \otimes \mathbf{y} - 3\mathbf{y} \otimes \mathbf{x} \otimes \mathbf{x}) \quad (1)$$

in case (a), while after rotation by an angle  $\theta$  with respect to an axis perpendicular to the molecular plane, as shown in case (b), it becomes

$$\begin{aligned} \beta = \beta_0[\cos 3\theta(\mathbf{y} \otimes \mathbf{y} \otimes \mathbf{y} - 3\mathbf{y} \otimes \mathbf{x} \otimes \mathbf{x}) \\ + \sin 3\theta(\mathbf{x} \otimes \mathbf{x} \otimes \mathbf{x} - 3\mathbf{x} \otimes \mathbf{y} \otimes \mathbf{y})]. \end{aligned} \quad (2)$$

In the general case of a planar molecule with *mm*2 symmetry, such as *p*-nitroaniline, the two in-plane components, namely  $\beta_{yyy}$  and  $\beta_{yxx}$  in case (a) can be independently manipulated; they can reach magni-

tudes comparable with  $\beta_{yxx}$  and can sometimes be made to surpass  $\beta_{yyy}$  (Nalwa, Nakajima, Watanabe, Nakamura, Yamada & Miyata, 1991). In the special case of  $D_{3h}$  symmetry, one has exactly  $\beta_{yxx} = -\beta_{xxx}$ . The situation from an experimental point of view is, however, more complex than that in the case of dipolar systems: as already pointed out, much of the predictive power of molecular engineering is based on the possibility of performing molecular EFISH measurements sequentially in solution and subsequent crystalline second harmonic generation (SHG) experiments with a coherent linkage ensured by the oriented gas model. In the case of octupolar dipolarless entities, the very absence of a dipole moment as well as the cancellation of the vector part of  $\beta$  precludes dipolar Langevin coupling as takes place in EFISH experiments, otherwise leading to the scalar quantity  $\beta \cdot \mu$ . A relevant strategy initiated in this work and intended to bypass this difficulty and reach the microscopic  $\beta$  tensor proceeds along the following lines: definition and growth of adequately oriented crystals built up from such systems; measurement of the  $\chi^{(2)}$  or  $d$  crystalline SHG tensor coefficients and evaluation of a  $\beta$  coefficient from an 'inverted' oriented gas model. A similar approach was used for the chiral *p*-nitroaniline derivative methyl (2,4-dinitrophenyl)aminopropanoate (MAP) (Oudar & Zyss, 1982), which allowed the evaluation of the four  $\beta$  coefficients of the corresponding planar asymmetric  $\pi$ -conjugated system. The present study aims to initiate this strategy in the context of octupolar species by: (i) definition of a crystalline system built up from encompassing nonlinear octupoles; (ii)

determination of the crystallographic structure, which will subsequently enable  $\beta$  and  $\chi^{(2)}$  to be related *via* an oriented gas model.

An adequately oriented structure refers to a stacking of molecular octupoles that will promote at the macroscopic crystalline level, hopefully in an optimal way, the microscopic octupolar hyperpolarizability. Such a geometric framework, generalizing from that established in the case of dipolar anisotropic one-dimensional systems (Zyss & Oudar, 1982), will be developed in the final section for the present case of  $D_{3h}$  planar systems stacked in an orthorhombic 222 structure.

Guanidinium, besides its easy availability, has a number of advantages that make it an obvious molecular candidate to work with using the strategy described above.

Firstly, the cation conformation supported by many X-ray crystal structure investigations reveals three equivalent C—N bond lengths of 1.325 (6) Å and N—C—N bond angles of 120° indicating perfect threefold symmetry ( $D_{3h}$ ). The short C—N bonds exhibit a pronounced electron-acceptor  $\pi$ -bond character while NH<sub>2</sub> is a classical donor group. Guanidinium thus appears as a polarizable acentric two-dimensional cation to be regarded as a planar octupolar chemical entity. The use of octupolar organic molecules and ions in the engineering of quadratic nonlinear-optical materials, although recognized only recently as such, has already been exemplified by triaminotrinitrobenzene (TATB), an acentric organic charge-transfer molecule (Ledoux, Zyss, Siegel, Brienne & Lehn, 1990) and is implicit in the B<sub>3</sub>O<sub>6</sub><sup>3-</sup> cyclic metaborate anion of the low-temperature form of BaB<sub>2</sub>O<sub>4</sub> (BBO) (Lu, Ho & Huang, 1982; Fröhlich, 1984; Chen, Wu, Jiang & You, 1984, 1985) or merely in the BO<sub>3</sub><sup>3-</sup> anion of Ca<sub>5</sub>(BO<sub>3</sub>)<sub>3</sub>F (Lei, Huang, Zheng, Jiang & Chen, 1989).

One may also identify a guanidinium-like fragment as being the active part of the substituted L-argininium phosphate monohydrate crystal (Aoki, Nagano & Iitaka, 1971; Eimerl, Velsko, Davis, Wang, Loicono & Kennedy, 1989).

Secondly, from the chemical point of view, guanidine is a strong Lewis base and the guanidinium cation may be easily anchored onto numerous inorganic and organic anions and polyanions through hydrogen-bonding networks.

Two natural synthesis pathways can be followed: (i) decomposition of guanidinium carbonate by the acid that bears the future anion or polyanion; (ii) precipitation of silver chloride through a chemical reaction between guanidinium chloride and silver salts containing the anions or polyanions to be combined. The latter route is recommended when the corresponding acids are unknown.

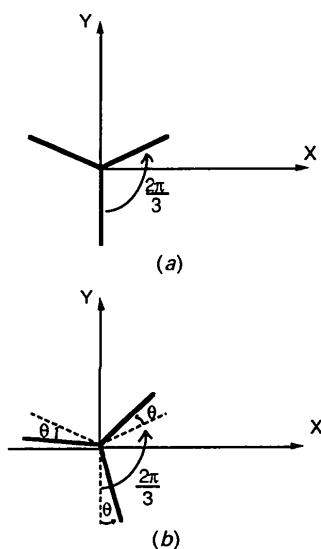


Fig. 1. The Y shape symbolizes the essential symmetry feature of an octupolar  $D_{3h}$  planar prototype system such as TATB or the guanidinium ion. (a) Reference framework reflecting the  $mm2$  subsymmetry of a  $D_{3h}$  system. In (b) the molecule is rotated parallel to its plane by an angle  $\theta$ .

## Chemical synthesis

Rapid scanning of the guanidinium carbonate/L-tartaric acid (water) phase diagram was carried out. Crystallization conditions are listed in Table 1. All solutions were crystallized at room temperature by slow evaporation. Two phases are singled out. The first,  $2\text{CH}_6\text{N}_3 \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$  of  $P2_1$  symmetry has already been extensively studied (Krumbe, Haussühl & Fröhlich, 1989). The second,  $\text{CH}_6\text{N}_3 \cdot \text{C}_4\text{H}_5\text{O}_6$ , was fully characterized by X-ray analysis (powder diffractogram, film method, four-circle diffractometry). Orthorhombic prisms up to  $15 \times 10 \times 5$  mm in size were grown. The chemical formula was established on the basis of the crystal structure determination.

The X-ray powder diffractogram was indexed. Cell parameters were refined by a least-squares method using angular data of 38 intensities collected between  $10$  and  $45^\circ 2\theta$ ,  $\lambda(\text{Cu } K\alpha) = 1.5418 \text{ \AA}$ . The cell parameters were  $a = 11.384 (8)$ ,  $b = 11.164 (7)$ ,  $c = 6.685 (4) \text{ \AA}$ .

## X-ray structure analysis data

For data collection a single crystal of size  $0.32 \times 0.48 \times 0.80$  mm was used. Orthorhombic unit-cell parameters were refined by a least-squares method using the angular data of 20 reflections ( $12 < \theta < 15^\circ$ ) measured with a four-circle diffractometer:  $a = 11.347 (2)$ ,  $b = 11.162 (2)$ ,  $c = 6.668 (2) \text{ \AA}$ ,  $V = 844.5 (5) \text{ \AA}^3$ ,  $Z = 4$ ,  $M_r = 209.16$ , space group  $P2_12_12_1$ ,  $D_x = 1.645 \text{ g cm}^{-3}$ ,  $F(000) = 440$ . Data collection conditions: Philips PW1100 diffractometer, graphite monochromator,  $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$ .  $\mu = 1.624 \text{ cm}^{-1}$ .  $\omega$  scan, scan width  $1.20^\circ$ , scan speed  $0.03^\circ \text{ s}^{-1}$ . The total background measuring time was 10 s. 1307 reflections were measured between  $3$  and  $35^\circ \theta$ ; 1307 unique;  $h_{\text{max}} = 18$ ,  $k_{\text{max}} = 18$ ,  $l_{\text{max}} = 11$ . Intensity reference reflections 410 and 442 showed no significant variation. Lorentz and polarization corrections were made, but no absorption correction was applied. Secondary-extinction correction:  $g = 6.575 \times 10^{-6}$  (Stout & Jensen, 1968). The structure was solved by direct methods with use of *MULTAN77* (Main, Lessinger, Woolfson, Germain & Declercq, 1977). H atoms were located by difference Fourier syntheses. Anisotropic full-matrix least-squares refinements were performed on  $F$ , using the weighting scheme  $w = 1/\sigma^2(F_o)$ , with  $\sigma^2(F_o)$  derived from  $4F_o^2/[\sigma^2(I_o) + (pF_o^2)^2]$  where  $p = 0.01$ . H atoms isotropically refined. Refined parameters: 172. Final refinement with 1229 independent reflections with  $I_o > 2\sigma(I_o)$ .  $R_{\text{int}} = 0.036$ . Final  $R = 0.049$ ,  $wR = 0.030$ ,  $S = 1.44$ . Maximum shift/e.s.d. = 0.01. Maximum peak height in the final difference Fourier map:  $0.33 \text{ e \AA}^{-3}$ . Scattering factors for neutral atoms and  $f'$ ,  $f''$  from *International Tables for X-ray Crystallog-*

Table 1. Crystallization conditions

Guanidinium carbonate	L-Tartaric acid (mol) [15 cm <sup>3</sup> (water)]	Observed crystalline phases
0.02	0.01	Guanidinium carbonate + guanidinium L-tartrate monohydrate
0.01	0.01	Guanidinium L-tartrate monohydrate (Krumbe, Haussühl & Fröhlich, 1989)
0.01	0.02	Guanidinium L-monohydrogentartrate
0.01	0.03	Guanidinium L-monohydrogentartrate + L-tartaric acid

Table 2. Atom parameters and their standard deviations

$B_{\text{eq}}$  is given for non-hydrogen atoms,  $B_{\text{iso}}$  for hydrogen atoms.

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}$ , $B_{\text{iso}}$ ( $\text{\AA}^2$ )
C(1)	0.3083 (2)	0.6015 (2)	0.9351 (4)	2.20 (4)
N(2)	0.4089 (2)	0.6572 (2)	0.9606 (3)	2.70 (4)
N(1)	0.3055 (2)	0.4837 (2)	0.9193 (4)	3.34 (5)
N(3)	0.2092 (2)	0.6629 (2)	0.9195 (4)	3.58 (5)
H(1)	0.236 (2)	0.443 (2)	0.912 (3)	2.8 (5)
H(2)	0.373 (1)	0.452 (2)	0.907 (3)	1.6 (4)
H(3)	0.207 (2)	0.736 (2)	0.922 (3)	2.5 (5)
H(4)	0.131 (2)	0.626 (2)	0.910 (4)	6.5 (8)
H(5)	0.471 (2)	0.612 (2)	0.983 (3)	2.9 (5)
H(6)	0.416 (2)	0.728 (2)	0.974 (4)	4.0 (6)
C(2)	0.0258 (2)	0.2907 (2)	1.0151 (3)	1.74 (4)
C(3)	0.1002 (2)	0.1802 (2)	1.0554 (4)	1.65 (4)
C(4)	0.1272 (2)	0.1161 (2)	0.8564 (4)	1.80 (4)
C(5)	0.2000 (2)	0.0044 (2)	0.8994 (4)	1.83 (4)
O(1)	-0.0850 (1)	0.2797 (1)	1.0669 (3)	2.49 (3)
O(2)	0.0672 (1)	0.3802 (1)	0.9401 (3)	2.60 (3)
O(3)	0.0417 (1)	0.1045 (1)	1.1912 (3)	2.56 (3)
O(4)	0.0197 (1)	0.0893 (1)	0.7599 (3)	3.05 (4)
O(5)	0.1503 (1)	-0.0942 (1)	0.8959 (3)	3.03 (4)
O(6)	0.3090 (1)	0.0195 (1)	0.9352 (3)	2.21 (3)
H(7)	0.372 (2)	0.146 (2)	0.969 (4)	4.8 (7)
H(8)	0.174 (1)	0.209 (2)	0.100 (3)	0.7 (4)
H(9)	0.173 (1)	0.167 (2)	0.779 (3)	1.4 (5)
H(10)	0.024 (2)	0.027 (2)	0.697 (4)	6.1 (7)
H(11)	0.085 (2)	0.074 (2)	0.266 (4)	5.4 (7)

raphy (1974, Vol. IV, Table 2.2C). *SDP* (Enraf-Nonius, 1977) was used for all calculations on a MicroVAXII. The structure was drawn using the *ORTEP* program (Johnson, 1965). The results are listed in Table 2.\*

## Description

Two helical chains formed through the aggregation of L-monohydrogentartrate anions located at  $y = \frac{1}{4}$ ,  $z = 0$  and  $y = \frac{3}{4}$ ,  $z = \frac{1}{2}$  run along the  $\mathbf{a}$  direction (Fig. 2). Every chain is built up through short hydrogen

\* Lists of anisotropic displacement parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55567 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA0280]

bonds that connect contiguous carboxylic groups [ $D-A = 2.544(2) \text{ \AA}$ ]. The hydroxyl groups of an L-monohydrogentartrate unit are hydrogen donors towards carboxylic groups belonging to two independent anion chains translated by  $c$  (Fig. 3). Every chain is connected to four adjacent ones delimiting large cavities at the intersections of two channels running along the  $a$  and  $c$  directions, which host the guanidinium cations (Fig. 4). This type of anionic subnetwork (which is due to the ability of L-monohydrogentartrate anions to self-aggregate) has been observed in tartrate structures containing large organic cations. Neutron diffraction structural studies have already displayed the aggregation of D-tartaric acid molecules through short hydrogen bonds (Okaya, Stemple & Kay, 1966; Albertsson, Oskarson & Stahl, 1979). This property seems preserved in tartaric acid salts (Bohaty & Fröhlich, 1983). The minimum space occupied by guanidinium cations in the intersecting channels can be estimated

from the radius  $R[C(1)-H(4)] = 2.03(2) \text{ \AA}$ , increased from the van der Waals hydrogen radius ( $1 \text{ \AA}$ ) to  $3.03 \text{ \AA}$ . The minimum diameter of the channel parallel to  $c$  is  $6.06 \text{ \AA}$  [ $C(1)-H(4)$  is the longest  $C(1)-H$  distance in the guanidinium cation]. Guanidinium cations are anchored onto the anionic subnetwork through hydrogen bonds (see Table 3 and Fig. 5), one of them bifurcated. The  $z$  altitudes of the guanidinium planes are close to 0.05, 0.45, 0.55 and 0.95. Such a cationic network (Fig. 6) contains pseudo-centres of symmetry. This is in agreement with the relatively weak SHG powder test (Kurtz & Perry, 1968) observed on a sample illuminated by YAG:Nd<sup>3+</sup> laser radiation at  $1.06 \mu\text{m}$ . The magnitude of the second-harmonic signal is of the same order as that of urea. In fact, closer inspection of the structure shows that the cation planes (Table 4) are not exactly perpendicular to the  $c$  axis, leading to a non-negligible contribution of microscopic hyperpolarizabilities to the macroscopic  $\chi^{(2)}$

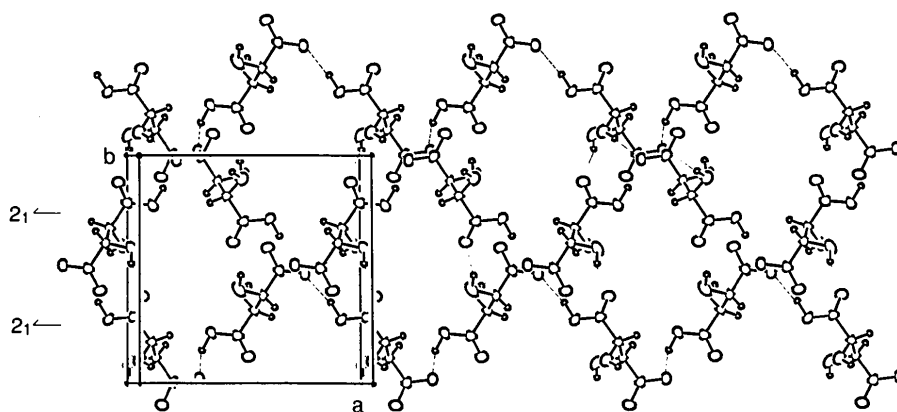


Fig. 2. Helical chains built up from the aggregation of L-monohydrogentartrate anions running along the  $a$  direction. Channels parallel to  $c$  are apparent.

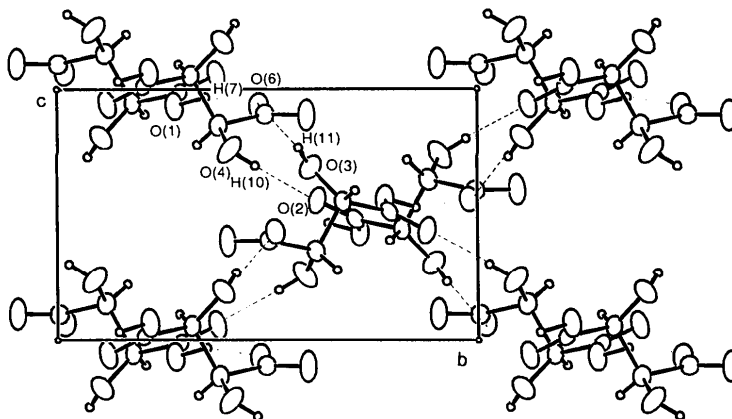


Fig. 3. Autoaggregation of anion chains inducing channels parallel to  $a$ .

tensor and hence a nonvanishing SHG signal. The dihedral angle between the guanidinium plane and the  $ab$  plane is about  $8^\circ$ .

The orientated gas model (Zyss & Oudar, 1982) provides an adequate framework allowing the microscopic hyperpolarizability  $\beta$  of the octupolar guanidinium cations to be related to the crystalline quadratic susceptibility tensor  $d$ . The general expression for the  $\beta$  hyperpolarizability tensor of purely octupolar  $J=3$  planar symmetry, given by (1), is a

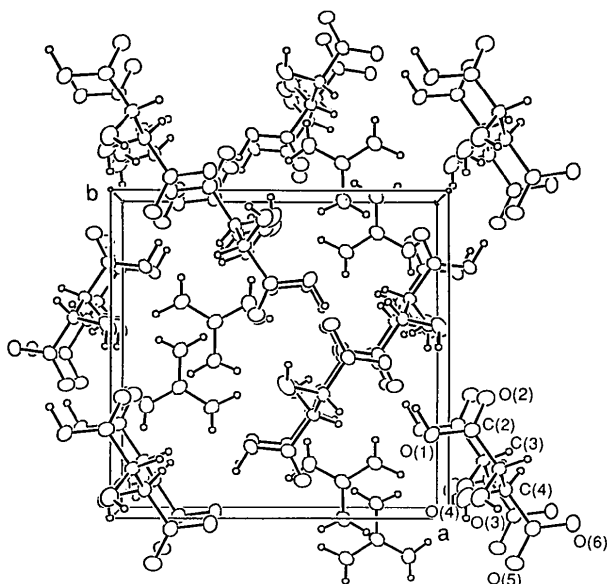


Fig. 4.  $ab$  projection displaying the encapsulation of guanidinium cations in channels parallel to  $c$ .

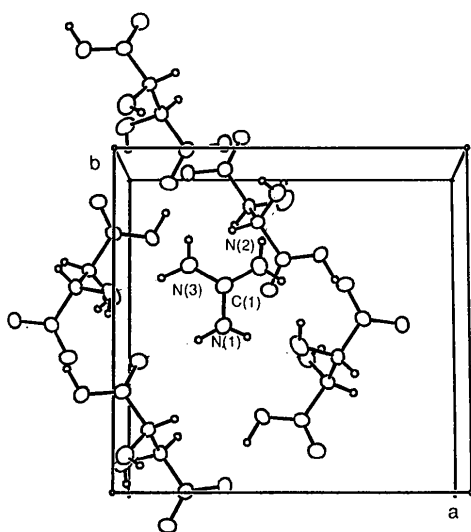


Fig. 5. Hydrogen-bond scheme of the guanidinium cation viewed along the  $c$  direction.

one-dimensional tensor that leads, after rotation, to the single nonvanishing  $b$  tensor coefficient in the orthorhombic 222 point-group symmetry assuming the validity of Kleinman conditions.  $b$  has been defined by Zyss & Oudar (1982) as the crystalline nonlinearity per molecule with local field corrections at this stage. We shall restrict the analysis to the geometry of current interest, whereby the angular deviation from the molecular  $\{xyz\}$  to the crystalline  $\{XYZ\}$  frames is small and cosine projection factors are accordingly approximated by their first-order expansions. The octupoles are oriented with respect to the molecular framework as shown in Fig. 1(a), the projection cosines of  $x$ ,  $y$  and  $z$  being respectively:

$$x = \cos\alpha'X + \cos\beta'Y + \cos\gamma'Z; \quad (3)$$

$$y = \cos\alpha''X + \cos\beta''Y + \cos\gamma''Z; \quad (4)$$

$$z = \cos\alpha X + \cos\beta Y + \cos\gamma Z. \quad (5)$$

The assumption of small angular deviations means that  $x$ ,  $y$  and  $z$  are respectively close to  $X$ ,  $Y$  and  $Z$  and leads to the following simplified expressions:

$$x = X - \Delta\beta'Y + \Delta\alpha Z; \quad (6)$$

$$y = \Delta\beta'X + Y + \Delta\beta Z; \quad (7)$$

$$z = -\Delta\alpha X - \Delta\beta Y + Z; \quad (8)$$

where

$$\alpha' = \Delta\alpha', \quad \beta' = \pi/2 + \Delta\beta', \quad \gamma' = \pi/2 + \Delta\gamma',$$

$$\alpha'' = \pi/2 + \Delta\alpha', \quad \beta'' = \Delta\beta'', \quad \gamma'' = \pi/2 + \Delta\gamma'',$$

$$\alpha = \pi/2 + \Delta\alpha, \quad \beta = \pi/2 + \Delta\beta, \quad \gamma = \Delta\gamma.$$

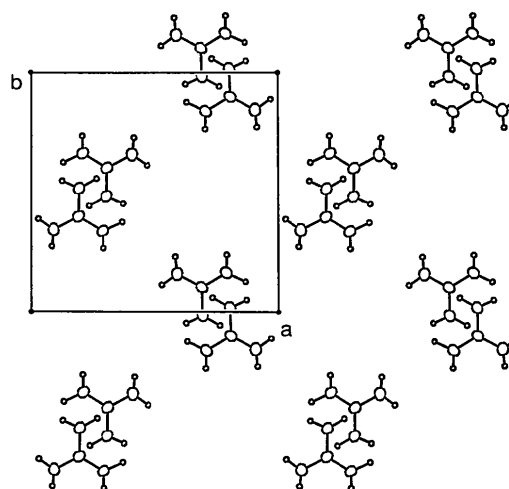


Fig. 6. Subnetwork of guanidinium cations ( $D_{3h}$ ), which appears to form a quasi-centrosymmetrical packing in an  $ab$  projection. In fact, the cation planes are not exactly perpendicular to  $c$  ( $8^\circ$  inclination).

Table 3. Main interatomic distances (Å) and bond angles (°) and their e.s.d.'s

## L-Monohydrogentartrate anion

C(2)—C(3)	1.519 (3)	C(3)—C(2)—O(1)	114.3 (2)
C(2)—O(1)	1.309 (3)	C(3)—C(2)—O(2)	121.8 (2)
C(2)—O(2)	1.212 (3)	O(1)—C(2)—O(2)	123.9 (2)
C(3)—C(4)	1.538 (3)	C(2)—C(3)—C(4)	109.7 (2)
C(3)—O(3)	1.406 (3)	C(2)—C(3)—O(3)	109.9 (2)
C(3)—H(8)	0.94 (2)	C(2)—C(3)—H(8)	105 (1)
		C(4)—C(3)—O(3)	111.7 (2)
C(4)—C(5)	1.523 (3)	C(4)—C(3)—H(8)	105 (1)
C(4)—O(4)	1.412 (3)	O(3)—C(3)—H(8)	115 (1)
C(4)—H(9)	0.92 (2)		
C(5)—O(5)	1.237 (3)	C(3)—C(4)—C(5)	109.1 (2)
C(5)—O(6)	1.271 (1)	C(3)—C(4)—O(4)	108.6 (2)
		C(3)—C(4)—H(9)	108 (1)
O(1)—H(7)	0.99 (2)	C(5)—C(4)—O(4)	112.4 (2)
O(3)—H(11)	0.78 (2)	C(5)—C(4)—H(9)	108 (1)
O(4)—H(10)	0.81 (3)	O(4)—C(4)—H(9)	111 (1)
		C(4)—C(5)—O(5)	118.5 (2)
		C(4)—C(5)—O(6)	117.0 (2)
		O(5)—C(5)—O(6)	124.4 (2)
		C(2)—O(1)—H(7)	109 (1)
		C(3)—O(3)—H(11)	112 (2)
		C(4)—O(4)—H(10)	111 (2)

## Guanidinium cation

C(1)—N(1)	1.320 (3)	N(1)—C(1)—N(2)	120.2 (2)
C(1)—N(2)	1.311 (3)	N(1)—C(1)—N(3)	119.4 (2)
C(1)—N(3)	1.321 (3)	N(2)—C(1)—N(3)	120.4 (2)
N(1)—H(1)	0.92 (1)	C(1)—N(1)—H(1)	121 (1)
N(1)—H(2)	0.85 (2)	C(1)—N(1)—N(2)	113 (1)
N(2)—N(5)	0.88 (2)	H(1)—N(1)—H(2)	124 (2)
N(2)—H(6)	0.80 (2)	C(1)—N(2)—H(5)	116 (1)
N(3)—H(3)	0.82 (2)	C(1)—N(2)—H(6)	125 (1)
N(3)—H(4)	0.98 (2)	H(5)—N(2)—H(6)	118 (2)
		C(1)—N(3)—H(3)	123 (1)
		C(1)—N(3)—H(4)	124 (1)
		H(3)—N(3)—H(4)	114 (2)

## Hydrogen bonds

	D—A	D—H	H—A	D—H—A
N(1)—H(1)···O(2)	2.944 (2)	0.92 (2)	2.04 (2)	167 (2)
N(1)—H(2)···O(3)	2.949 (2)	0.84 (2)	2.12 (2)	166 (2)
N(2)—H(5)···O(5)	2.985 (2)	0.88 (2)	2.20 (2)	149 (2)
N(2)—H(6)···O(3)	3.259 (3)	0.80 (2)	2.69 (2)	129 (2)
N(2)—H(6)···O(4)	3.556 (3)	0.80 (2)	2.88 (2)	143 (2)
N(3)—H(3)···O(5)	2.797 (2)	0.82 (2)	2.01 (2)	162 (2)
N(3)—H(4)···O(4)	2.976 (2)	0.98 (2)	2.10 (3)	149 (2)
O(1)—H(7)···O(6)	2.544 (2)	0.99 (2)	1.60 (2)	158 (2)
O(3)—H(11)···O(6)	2.725 (2)	0.78 (2)	1.95 (2)	173 (3)
O(4)—H(10)···O(2)	2.864 (2)	0.81 (3)	2.15 (3)	147 (2)

The  $\Delta$  notation refers to small angles. Orthogonality conditions have helped reduce the number of small-angle parameters from nine to three, namely  $\Delta\alpha$ ,  $\Delta\beta$  and  $\Delta\beta'$ .

Equations (6)–(8) can then be fed into tensor  $\beta$  as given by (1), leading to its rotated version  $b$  in the crystalline  $\{XYZ\}$  frame, by multilinear development of the tensorial products (Schwartz, 1981)

$$\begin{aligned} \mathbf{b}/\beta_0 = & (\Delta\beta' \mathbf{X} + \mathbf{Y} + \Delta\beta \mathbf{Z}) \otimes [(\Delta\beta' \mathbf{X} + \mathbf{Y} \\ & + \Delta\beta \mathbf{Z}) \otimes (\Delta\beta' \mathbf{X} + \mathbf{Y} + \Delta\beta \mathbf{Z}) - 3(\mathbf{X} \\ & - \Delta\beta' \mathbf{Y} + \Delta\alpha \mathbf{Z}) \otimes (\mathbf{X} - \Delta\beta' \mathbf{Y} + \Delta\alpha \mathbf{Z})]. \end{aligned} \quad (9)$$

Tensorial products are symmetric in nonresonant cases (Kleinman conditions) and terms containing

Table 4. Least-squares-plane orthonormal equation for the guanidinium cation

$$0.122 (2)X + 0.067 (2)Y - 0.9903 (2)Z = -5.29 (1),$$

based on  $a, b, c$  axes.  $X, Y, Z$  in Å.

Shifts (Å) of atoms used to find the least-squares plane orthonormal equation

$$\begin{array}{cc} \text{C}(1) & -0.009 (3) & \text{N}(2) & 0.003 (2) \\ \text{N}(1) & 0.003 (3) & \text{N}(3) & 0.003 (3) \end{array}$$

Shifts (Å) of H atoms in guanidinium plane

$$\begin{array}{cc} \text{H}(1) & -0.07 (2) & \text{H}(4) & -0.07 (3) \\ \text{H}(2) & 0.16 (2) & \text{H}(5) & -0.09 (2) \\ \text{H}(3) & 0.04 (2) & \text{H}(6) & -0.02 (2) \end{array}$$

Direction cosines of the normal to the least-squares plane

$$N(\alpha = 97, \beta = 93.8, \gamma = 8^\circ)$$

angular deviations of degree higher than one (second-order infinitesimal quantities) are neglected. Furthermore, we may limit the development to  $\mathbf{X} \otimes \mathbf{Y} \otimes \mathbf{Z}$  coefficients, as the only nonvanishing crystalline coefficient in the 222 symmetry is  $b_{XYZ}$  ( $b_{14} = b_{25} = b_{36}$  in contracted notation) (Yariv, 1989). These conditions greatly simplify the algebraic development, reducing  $\mathbf{b}$  to

$$\mathbf{b} = b_{XYZ} \mathbf{X} \otimes \mathbf{Y} \otimes \mathbf{Z} = -6\Delta\alpha\beta_0 \mathbf{X} \otimes \mathbf{Y} \otimes \mathbf{Z}. \quad (10)$$

A striking consequence of these considerations is that, within the small-angular-rotation approximation, only the  $\Delta\alpha$  rotation of the octupole around its symmetry axis  $y = Y$  will contribute to the crystalline  $b$  tensor. Such a  $\Delta\alpha$  rotation refers to 'rolling' of the octupolar plane while  $\Delta\beta$  is a 'pitch' angle and  $\Delta\beta'$  is the simpler in-plane rotation shown in Fig. 7. Equation (10) clearly expresses the detrimental influence of a small roll angle  $\Delta\alpha$  (see Fig. 7) and explains the relatively weak intensity of the SHG powder signal.

It is worthwhile generalizing the above analysis to arbitrary independent rotations of eventually large amplitudes around  $\mathbf{X}, \mathbf{Y}$  and  $\mathbf{Z}$  defined by the angles  $\varphi$  (around  $\mathbf{X}$ ),  $\theta$  (around  $\mathbf{Y}$ ) and  $\psi$  (around  $\mathbf{Z}$ ). We restrict the following analysis to independent

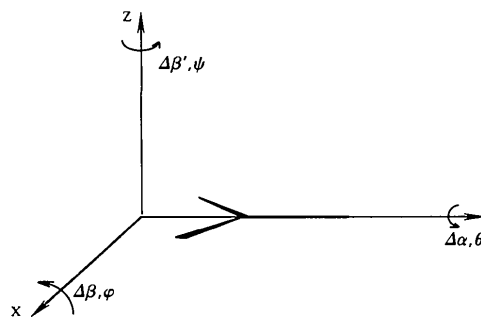


Fig. 7. Conventions defining the rotations of the guanidinium plane with respect to the principal crystalline dielectric axes.  $\Delta$  indicates small angles.

rotations and point group 222. A more general analysis (*cf.* Zyss, 1991a), outside the scope of this paper, will be published elsewhere.

*Rotation by  $\theta$  around Y.* ('Rolling' motion generalizing over  $\Delta\alpha$  for large amplitudes.) The derivation is similar to that previously detailed for small rotations where all tensorial projection cosines are retained using

$$\mathbf{y} = \mathbf{Y}, \quad (11)$$

$$\mathbf{x} = \cos\theta\mathbf{X} + \sin\theta\mathbf{Z}, \quad (12)$$

$$\mathbf{b}/\beta_0 = \mathbf{Y} \otimes [\mathbf{Y} \otimes \mathbf{Y} - 3(\cos\theta\mathbf{X} + \sin\theta\mathbf{Z}) \otimes (\cos\theta\mathbf{X} + \sin\theta\mathbf{Z})], \quad (13)$$

$$\mathbf{b} = -6\beta_0 \sin\theta \cos\theta \mathbf{X} \otimes \mathbf{Y} \otimes \mathbf{Z}, \quad (14)$$

where coefficients other than  $\mathbf{X} \otimes \mathbf{Y} \otimes \mathbf{Z}$  were neglected. The 'optimal'  $b_{XYZ}$  magnitude is then obtained for  $\theta = \pi/4$  as shown in Fig. 8. In this geometry, the two octupolar planes are perpendicular to each other with the rotation axis along a common twofold molecular symmetry axis, leading to a highly symmetric but noncentrosymmetric bimolecular structure. The optimal  $b$  coefficient is then given by

$$b_{\text{opt}} = -3\beta_0 \mathbf{X} \otimes \mathbf{Y} \otimes \mathbf{Z}.$$

*Rotation by  $\varphi$  around X.* ('Pitch' motion generalizing over  $\Delta\beta$  for large amplitudes.) We now have

$$\mathbf{x} = \mathbf{X}, \quad (15)$$

$$\mathbf{y} = \cos\varphi\mathbf{Y} + \sin\varphi\mathbf{Z}, \quad (16)$$

$$\mathbf{b}/\beta_0 = (\cos\varphi\mathbf{Y} + \sin\varphi\mathbf{Z}) \otimes [(\cos\varphi\mathbf{Y} + \sin\varphi\mathbf{Z}) \otimes (\cos\varphi\mathbf{Y} + \sin\varphi\mathbf{Z}) - 3\mathbf{X} \otimes \mathbf{X}], \quad (17)$$

$$\begin{aligned} \mathbf{b}/\beta_0 = & \cos^3\varphi \mathbf{Y} \otimes \mathbf{Y} \otimes \mathbf{Y} + \sin^3\varphi \mathbf{Z} \otimes \mathbf{Z} \otimes \mathbf{Z} \\ & + 3\cos^2\varphi \sin\varphi \mathbf{Y} \otimes \mathbf{Y} \otimes \mathbf{Z} \\ & + 3\cos\varphi \sin^2\varphi \mathbf{Y} \otimes \mathbf{Z} \otimes \mathbf{Z} \\ & - 3\cos\varphi \mathbf{Y} \otimes \mathbf{X} \otimes \mathbf{X} - 3\sin\varphi \mathbf{Z} \otimes \mathbf{X} \otimes \mathbf{X}. \end{aligned} \quad (18)$$

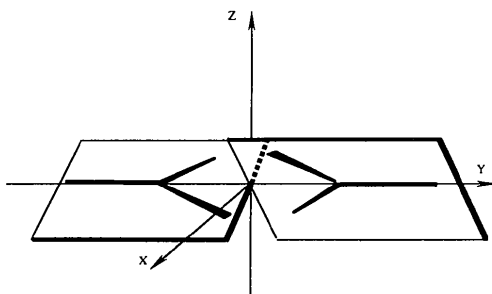


Fig. 8. Optimal noncentrosymmetric orientation of trigonal entities in the 222 crystalline unit cell for arbitrary rotations around the twofold crystalline symmetry axis  $Y$ , also taken as a common molecular twofold symmetry axis.

This expression does not contain any component along  $\mathbf{X} \otimes \mathbf{Y} \otimes \mathbf{Z}$ , which demonstrates that, even for large amplitude, 'pitching' around a twofold axis does not contribute to a crystalline coefficient in the 222 point-group symmetry.

*Rotation by  $\psi$  around Z.* (In-plane rotation around an axis perpendicular to the octupolar plane as in Fig. 1a.) This rotation does not contribute to the  $\mathbf{b}$  tensor since the 222 symmetry requires out-of-plane rotation to build up the single nonvanishing  $b_{XYZ}$  coefficient.

Finally, we are in a position to assess the adequacy of the actual guanidinium L-monohydrogentartrate structure for quadratic nonlinear optics by comparison with the optimal 222 structure obtained for  $\theta = \pi/4$ . A measure of the departure of the actual structure from the ideal one is the ratio  $b_{XYZ}/b_{XYZ}^{\text{opt}} = 2\Delta\alpha \approx 0.28$ . The  $b$  coefficient could thus be increased by a factor of four if the ideal geometry were reached by a more adequate hosting structure.

### Concluding remarks

The guanidinium L-monohydrogentartrate crystal exemplifies an attempt at organizing nonpolar octupolar nonlinear guanidinium cations in an oriented guest-host structure cross-linked by multidirectional hydrogen bonds. The host lattice is an aggregated L-monohydrogentartrate polyanionic chain shaping a double array of orthogonal channels that locate the guest cations at their intersections. This attempt has proved only partially successful as it falls somewhat short of the optimal symmetry requirements for an octupolar nonlinear crystal. We have shown that an improvement by a factor of four could be achieved within the same orthorhombic crystal point group by adequate modification of the guest sublattice. In future, two strategies will be pursued. Firstly, use of an octupolar and possibly trigonal host so as to match the symmetry of the octupolar guest and hopefully lock the guest sublattice in a macroscopic octupolar arrangement. Secondly, and in combination with the first strategy, a variety of octupolar guests, other than guanidinium, will be investigated in this context with the additional potential benefit of tuning both the transparency and efficiency of the resulting crystal.

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## Structures of Quinone Imine Metabolites Related to the Anti-Cancer Drug Amsacrine

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### Abstract

(5): *N*-(9-Acridinyl)-3-methoxy-1,4-benzoquinone monoimine,  $C_{20}H_{14}N_2O_2$ ,  $M_r = 314.3$ , monoclinic,  $P2_1/c$ ,  $a = 13.451$  (8),  $b = 7.007$  (4),  $c = 17.864$  (12) Å,  $\beta = 117.26$  (4)°,  $V = 1497$  (2) Å<sup>3</sup>,  $Z =$

4,  $D_m = 1.36$  (1),  $D_x = 1.395$  g cm<sup>-3</sup>,  $Mo K\alpha$ ,  $\lambda = 0.71069$  Å,  $\mu = 0.99$  cm<sup>-1</sup>,  $F(000) = 656$ ,  $T = 138$  (5) K,  $R = 0.049$  for 1556 reflections. (8): *N*-(9-Acridinyl)-2-methoxy-1,4-benzoquinone monoimine,  $C_{20}H_{14}N_2O_2$ ,  $M_r = 314.3$ , triclinic,  $P\bar{1}$ ,  $a = 9.365$  (1),  $b = 13.318$  (2),  $c = 6.918$  (3) Å,  $\alpha = 96.45$  (3),  $\beta =$