Investigation of Some New Nonlinear Optical Crystals by Means of NQR, IR and X-Ray Diffraction Methods*

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Z. Naturforsch. **53a,** 528 – 536 (1998); received January 26, 1998

Some new analogues of the nonlinear optical crystal L-arginine phosphate monohydrate (LAP) (Arg · HIO_3, Arg · $2HIO_3$, Lys · HIO_3, Lys · $2HIO_3$, Lys · $3HIO_3$, Bet · $3HIO_3$) were obtained and investigated by means of IR, NQR, X-ray diffraction and SHG methods. The importance of this class of crystals for revealing new nonlinear optical crystals is pointed out.

Introduction

The discovery in 1983 of the promising nonlinear optical and other properties [1] of crystalline L-arginine phosphate monohydrate (LAP) [3–7], (the symmetry and structure of which was determined earlier [2]) has lead to the search of analogues which might surpass LAP in some parameters [8–10]. In [8], an attempt was made to obtain LAP analogues by interaction of arginine with stoichiometric amounts of various acids. In some cases, the compounds had a very high solubility and formed viscous solutions. In iodic and some other acids, the compounds formed a very fine powder. From 10 analogues, the most attractive one was L-arginine fluoride Arg · HF. When trying to synthesize arginine monoarsenate, unexpectedly diarsenate Arg · $2H_3AsO_4$ was formed [8]. In addition, it was found, that the second harmonic generation (SHG) signal from most of the compounds with symmetry $P2_1$ was much more intensive than from the ones with symmetry $P2_12_12_1$.

Taking into account the ability of iodic acid to form acid salts [11–13], in addition to arginine iodate we tried to get its acid salts also [14]. Together with arginine iodate, the formation of arginine diiodate Arg · $2HIO_3$ in the system Arg + HIO_3 + H_2O was established which, contrary to Arg · HIO_3, crystallizes well. The interaction of arginine and some other amino acids with various inorganic acids, the role of the optical activity of amino acids, and the influence of symmetry on nonlinear optical properties seemed to be interesting.

Iodine-127 NQR, IR spectroscopy, X-ray diffraction and SHG methods were used.

Experimental Part

The amino acids (L-arginine, L-lysine, betaine) were purchased from the Institute of Research and Technology of Amino Acids (Yerevan). All compounds were synthesized by the interaction of water solutions of amino acids with inorganic acids in appropriate mole relations and subsequent evaporation at room temperature. IR spectra were registered on a Specord 75IR spectrophotometer at room temperature, using nujol mull or hexachlorbutadien. The NQR spectra were measured on an ISSh-2-13 pulsed spectrometer. The X-ray data were collected on an automatic diffractometer ENRAF-NONIUS CAD-4 (Mo K_α radiation, graphite monochromator). The structures were solved by the direct method and refined by the full-matrix least-squares technique with anisotropic thermal parameters for non-hydrogen atoms using the SHELXL-93 program. The SHG in powders and crystals was checked with use of YAG: Nd Q-switched laser (λ = 1.06 μm).

Results and Discussion

L-Arg · HIO_3

As was found in [8], the interaction of Arg (L-arginine, $NH_2C(NH)NH(CH_2)_3CH(NH_2)COOH$) with HIO_3 in the ratio 1:1 resulted in an extremely fine powder of Arg · HIO_3. Its IR spectrum is shown on Fig. 1 a, and the iodine-127 NQR frequencies measured at 77 K are pre-

* Presented at the XIVth International Symposium on Nuclear Quadrupole Interactions, Pisa, Italy, July 20–25, 1997.

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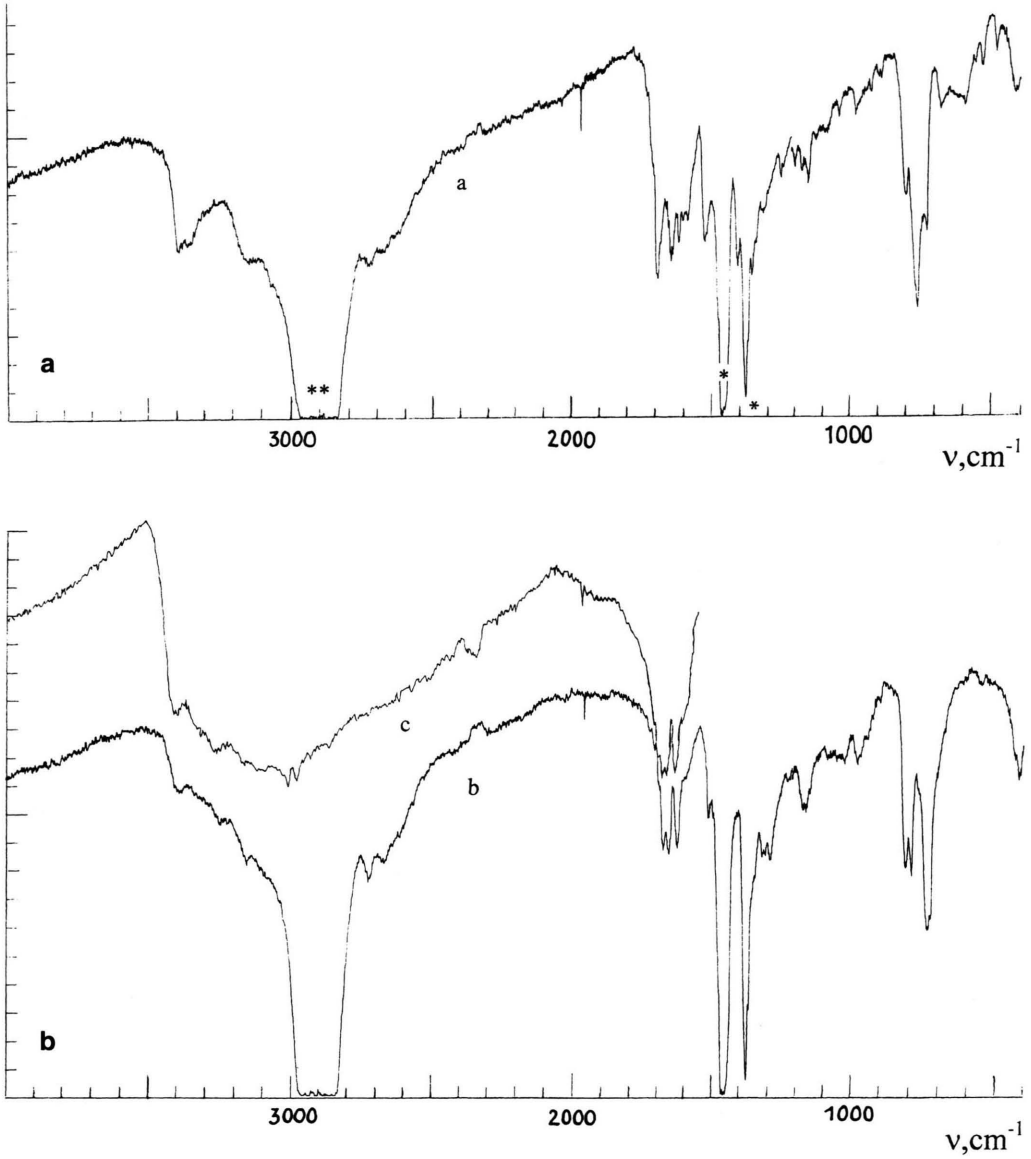

Fig. 1. The IR spectrum of Arg · HIO_3 (a) and Arg · $2HIO_3$ (b). The asterisks here and further designate of absorption bands of nujol. A part of the Arg · $2HIO_3$ spectrum in hexachlorbutadien (c) is also shown.

sented in Table 1. The NQR resonance lines were weak ($S/N \sim 2$) and broad. Nevertheless, they indicated a certain degree of crystallinity. The NQR frequencies, asymmetry parameters (η), and quadrupole coupling constants eQq_{zz} are typical for little distorted IO_3 groups [15]. The absorption band in the region 700–800 cm^{-1} of the Arg · HIO_3 IR spectrum concerns stretching vibrations of the IO_3 group. The absorption band of the COOH carboxyl group lies in the region of 1700 cm^{-1} and above, while the carboxylate group COO^- absorbs in the region of 1600 cm^{-1} and below. Rather strong hydrogen bonds can lower the frequencies of the COOH group and accordingly raise the frequencies of the COO^- group up to intermediate values.

Table 1. Iodine-127 NQR data at 77 K.

Compounds	ν_1, MHz	ν_2, MHz	η	eQq_{zz}, MHz
Arg · HIO_3	151.1	301	0.05	1004
Arg · $2HIO_3$	151.87	–	–	–
	–	–	–	–
Lys · $3HIO_3$	152.67	304.10	0.0561	1014.32
	155.69	305.33	0.1240	1020.93
	216.656	320.33	0.5488	1123.99
Bet · $3HIO_3$	163.606	312.29	0.1934	1048.73
	194.408	313.745	0.4451	1083.81
	205.84	325.73	0.4690	1129.11

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å $\times 10^3$] of L-Arg · $2HIO_3$. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U(eq)
I(1A)	17580(1)	–998(1)	3847(1)	27(1)
O(11)	19562(10)	–2124(10)	3576(3)	45(2)
O(12)	15607(9)	–2212(8)	3603(3)	42(2)
O(13)	17487(10)	717(7)	3365(2)	42(1)
I(2A)	12789(1)	–932(1)	4763(1)	26(1)
O(21)	14737(8)	465(7)	4594(2)	37(1)
O(22)	14052(10)	–2600(9)	5106(3)	56(2)
O(23)	11820(10)	191(10)	5336(3)	54(2)
O(1)	10310(9)	1568(7)	4280(3)	38(1)
O(2)	9259(9)	3330(7)	3651(3)	38(1)
C(1)	10366(11)	2904(9)	4035(3)	28(1)
C(2)	11878(14)	4217(10)	4155(3)	39(2)
N(4)	12839(9)	3825(7)	4674(2)	31(1)
C(3)	13618(20)	4000(22)	3708(5)	103(6)
C(4)	13292(26)	4121(29)	3253(7)	195(13)
C(5)	14629(13)	3985(16)	2805(4)	59(3)
N(3)	16260(9)	5077(9)	2847(3)	35(1)
C(6)	17638(11)	5080(10)	2484(3)	31(1)
N(1)	19234(9)	5951(11)	2565(3)	41(2)
N(2)	17477(11)	4159(10)	2038(3)	46(2)

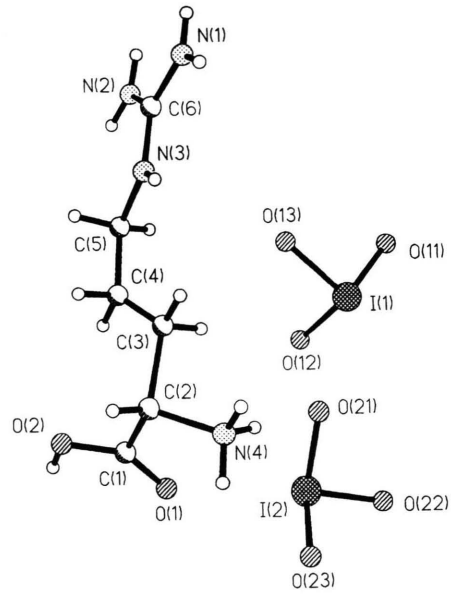

Fig. 2. The asymmetric part of the L-Arg · $2HIO_3$ unit cell.

Table 3. Bond lengths [Å] and angles (°) of Arg · $2HIO_3$.

I(1A)–O(11)	1.781(7)	O(11)–I(1A)–O(12)	101.0(3)
I(1A)–O(12)	1.788(6)	O(12)–I(1A)–O(13)	98.9(3)
I(1A)–O(13)	1.829(5)	O(11)–I(1A)–O(13)	99.0(3)
I(2A)–O(21)	1.814(6)	O(23)–I(2A)–O(21)	100.2(3)
I(2A)–O(22)	1.790(6)	O(23)–I(2A)–O(22)	102.1(4)
I(2A)–O(23)	1.783(6)	O(22)–I(2A)–O(21)	102.0(3)
C(1)–O(1)	1.233(9)	O(1)–C(1)–O(2)	125.9(7)
C(1)–O(2)	1.277(10)	O(1)–C(1)–C(2)	121.6(7)
C(1)–C(2)	1.516(10)	O(2)–C(1)–C(2)	112.5(6)
C(2)–N(4)	1.495(9)	N(4)–C(2)–C(1)	109.7(6)
C(2)–C(3)	1.66(2)	N(4)–C(2)–C(3)	103.8(8)
C(3)–C(4)	1.16(2)	C(1)–C(2)–C(3)	107.5(7)
C(4)–C(5)	1.46(2)	C(2)–C(3)–C(4)	121(2)
C(5)–N(3)	1.435(11)	C(3)–C(4)–C(5)	128(2)
N(3)–C(6)	1.322(10)	C(4)–C(5)–N(3)	113.6(9)
C(6)–N(1)	1.326(19)	C(5)–N(3)–C(6)	121.5(7)
C(6)–N(2)	1.343(9)	N(1)–C(6)–N(2)	119.0(7)
N(1)–C(6)–N(3)	120.2(7)	N(3)–C(6)–N(2)	120.7(7)

L-Arg · 2HIO₃

The congruently soluble compound Arg · $2HIO_3$ crystallizes perfectly. A good optical quality crystal with a few centimeter size was grown by the temperature reduction method in the temperature range 40-15 °C. The IR spectrum of Arg · $2HIO_3$ is shown on Figure 1b. The absence of absorption bands in the region 600–700 cm^{-1}, relating to ν(I-OH) in the HIO_3 group, testifies its absence. Hence, on the basis of the IR spectrum it is possible to assume a protonation of the guanidyl and amino group and the existence of the COOH carboxyl group. However, the appropriate absorption is below 1700 cm^{-1} (what can evidence the intermediate character of the COOH group). The absorption close to 3000 cm^{-1} can be related to the stretching ν(CH), and in the range 3000–3500 cm^{-1} to the stretching ν(NH) and probably ν(OH). On the basis of these data it was possible to expect in the iodine-127 NQR spectrum one pair of resonant lines for each transition. However, to our surprise, despite the high quality of the Arg · $2HIO_3$ crystals, we have found only one weak and very broad ($\Delta\nu \approx 1.5$ MHz) line. This could testify the presence of internal motion broadening of the NQR lines. We determined the structure of Arg · $2HIO_3$ by X-ray diffraction. The number of collected reflections was 2181. The orthorhombic unit cell with dimensions: a = 6.9554(14) Å,

$b = 7.998(2)$ Å, $c = 25.038(5)$ Å contains four formula units, $D_m = 2.49$ (2) Mg/m^3, $D_c = 2.509$ Mg/m^3, space group $P2_12_12_1$. The atomic coordinates are collected in Table 2; bond lengths and angles are listed in Table 3. The asymmetric part of the unit cell contains an arginine molecule and two IO_3 groups. The bond lengths and angles in the iodate groups are usual for iodates and correspond to the IR spectrum. Despite the sufficiently low value of the R-factor ($R_1 = 0.0321$ and $wR_2 = 0.0981$ for all data), hydrogen atoms on the background of the heavy iodine atoms could not be located. In Fig. 2, the hydrogen atoms are added in the expected positions. The lengths of the C–OH and C=O bonds in the carboxyl group lie usually in the 1.298–1.320 Å and 1.203–1.224 Å intervals [16]. It is possible, however, that the atom O(2) is connected to hydrogen, and some shortening of C(1)–O(2) is probably explained by a hydrogen bond O(2)...O(13) of 2.530 Å. This bond extends also the I(1)–O(13) bond a little. Unusual are the lengths of the C(2)–C(3) and in particular the C(3)–C(4) bonds. Such anomaly is connected with disordering in the structure of Arg · $2HIO_3$, as confirmed by the high values of the equivalent isotropic and anisotropic displacement parameters of the atoms C(3) and in particular C(4). This internal motion can cause the unusual bonds in the arginine molecule and essentially the broadening of NQR lines, preventing their registration. In the arginine "molecule" of the L-Arg · $2HNO_3$ crystal, the detailed data of which will be presented separately, such anomalies are not observed.

Lys-HIO_3-H_2O

The synthesis of lisine iodate from this system is described in [17]. By our data, in this system a few compounds with the formula Lys · $nHIO_3$ are formed, where $n = 1, 2, 3$, and one more compound with $n > 3$, the composition of which is under study. From these, only Lys · $3HIO_3$ crystallizes well. The lisine molecule $H_2N(CH_2)_4CH(NH_2)COOH$, like arginine, has two functional groups, capable to protonation. There are compounds with the compositions Lys.HCl and Lys.2HCl. Similar compounds are formed with HIO_3. Lys · HIO_3, was obtained from a water solution at the ratio 1:1 of Lys and HIO_3. Its IR spectrum is shown on Figure 3. The strong absorption band in the region which is characteristic for the iodate group (740 cm^{-1}, 755 cm^{-1} and 806 cm^{-1}), and also the absence of absorption higher than 1600 cm^{-1} indicate protonation of both amino groups and transition of protons from HIO_3 and the own carboxyl group. The compound Lys · $2HIO_3$ can be obtained from a water solution with the stoichiometric ratio of Lys and HIO_3. Lys · $2HIO_3$ was received as a powder. The IR spectrum is shown on Figure 3b. A strong absorption band with peaks at 727; 753; 786 and 807 cm^{-1} is characteristic for iodate groups. The presence of the band close to 1687 cm^{-1} indicates that two amino groups are protonated owing to two protons of HIO_3 groups, and the own carboxyl COOH group is protonated. The absorption band at 3500 cm^{-1} is probably connected with ν(OH) of the COOH group.

The compound Lys · $3HIO_3$ can be prepared as needles or plates by evaporation of a solution with stoichiometric amounts of Lys and HIO_3. However it is possible to prepare bulk crystals by decreasing the temperature. The presence of the absorption band at 1713 cm^{-1} in the IR spectrum of Lys · $3HIO_3$ (Fig. 3c) indicates the existence of the COOH group. The band at 1600 cm^{-1} is related to bending vibrations of the NH_3^+ group. There are peaks with frequencies 815; 780; 740; 720; 680 and 613 cm^{-1} in the region of iodate group absorption. The presence of a band at 613 cm^{-1}, characteristic for stretching vibrations ν(I–OH), indicate the presence of the HIO_3 group. So, the interaction of lisine with three HIO_3 molecules results in protonation of lisine owing to two of them, and the third HIO_3 molecules remains as HIO_3 group. These conclusions prove to be true by the NQR data (Ta-

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) of L-Lys · $3HIO_3$.

Atom	x	y	z	U(eq)
I(1)	7240(1)	3828(1)	8742(1)	16(1)
O(11)	6527(8)	1946(11)	7880(4)	26(1)
O(12)	6660(8)	6270(11)	8169(4)	26(1)
O(13)	9336(5)	3776(14)	8507(4)	28(1)
I(2)	2251(1)	3579(1)	9341(1)	15(1)
O(21)	1524(7)	1153(11)	9821(5)	28(1)
O(22)	1510(7)	5336(13)	10289(4)	27(1)
O(23)	4277(6)	3537(11)	9774(4)	24(1)
I(3)	4320(1)	–863(1)	8169(1)	14(1)
O(31)	2990(7)	1453(10)	8057(4)	23(1)
O(32)	4450(7)	–1352(12)	7001(3)	22(1)
O(33)	2810(7)	–2824(10)	8399(4)	25(1)
O(1)	5864(7)	4468(14)	5196(4)	32(2)
O(2)	3679(7)	4472(15)	4265(4)	33(2)
C(1)	4459(9)	4389(14)	5065(4)	21(1)
C(2)	3304(8)	4029(15)	5828(4)	21(1)
C(3)	1906(9)	5578(15)	5788(5)	23(1)
C(4)	650(10)	5108(17)	6487(6)	28(2)
C(5)	–709(10)	6730(17)	6432(6)	30(2)
C(6)	–343(9)	8843(19)	6861(5)	29(2)
N(7)	–361(8)	8759(15)	7870(4)	26(1)
N(8)	4238(8)	4192(13)	6700(4)	22(1)

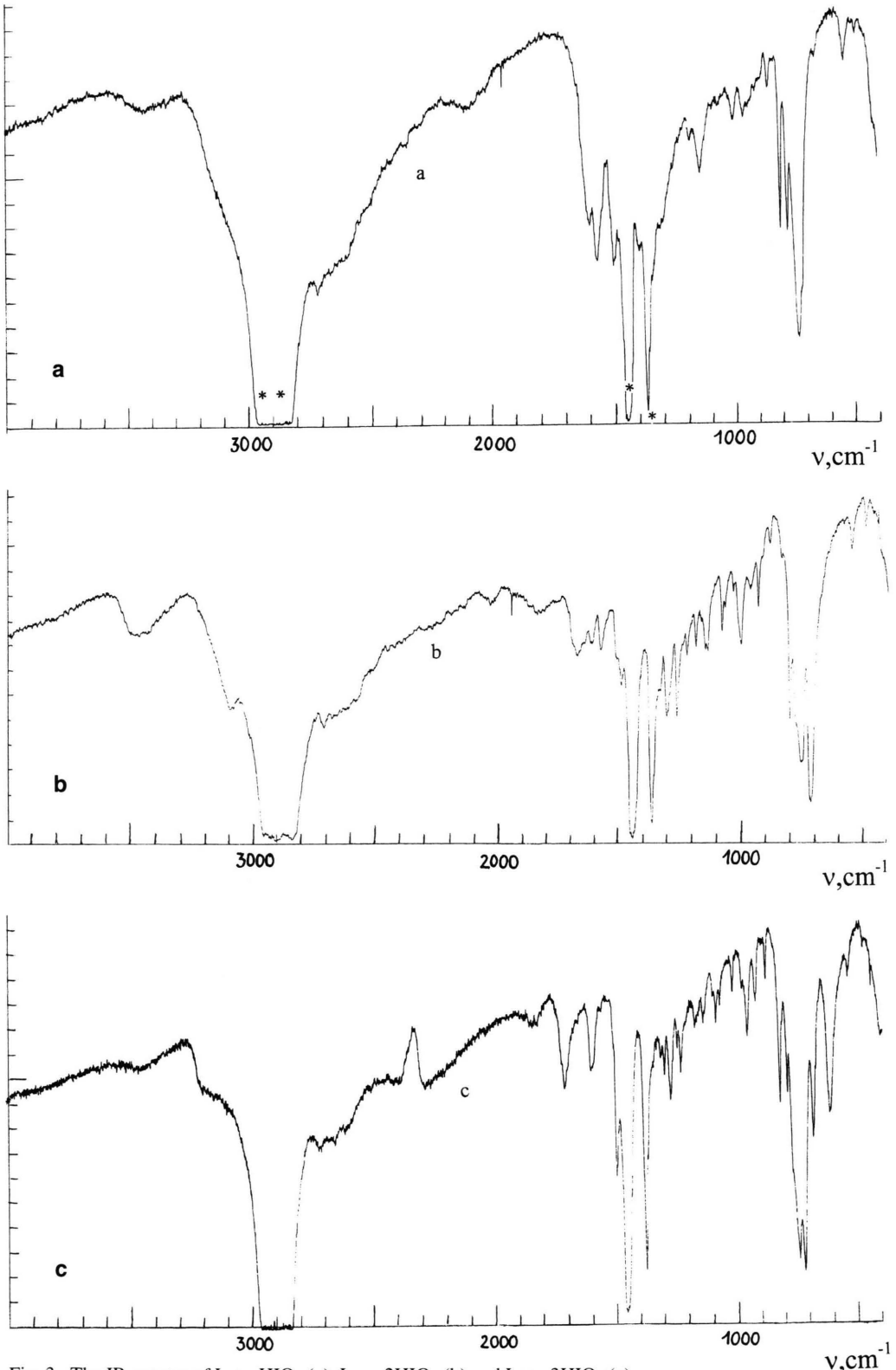

Fig. 3. The IR spectra of Lys · HIO_3 (a), Lys · $2HIO_3$ (b) and Lys · $3HIO_3$ (c).

Table 5. Bond lengths [Å] and angles (°) of Lys · $3HIO_3$.

I(1)–O(11)	1.821(6)	I(1)...O(21)	2.740
I(1)–O(12)	1.816(7)	I(1)...O(22)	2.805
I(1)–O(13)	1.804(5)	I(1)...O(23)	2.977
I(2)–O(21)	1.809(7)	I(2)...O(13)	2.677
I(2)–O(22)	1.914(6)	I(2)...O(33)	2.720
I(2)–O(23)	1.780(5)	I(2)...O(31)	2.429
I(3)–O(31)	1.845(6)	I(3)...O(11)	2.620
I(3)–O(32)	1.798(5)	I(3)...O(12)	2.670
I(3)–O(33)	1.806(6)	I(3)...O(23)	3.184
C(1)–O(1)	1.182(9)	C(1)–O(2)	1.320(9)
C(1)–C(2)	1.537(10)	C(2)–C(3)	1.524(11)
C(2)–N(8)	1.474(9)	C(3)–C(4)	1.538(11)
C(4)–C(5)	1.531(13)	C(5)–C(6)	1.50(2)
N(7)–C(6)	1.491(10)	N(7)–C(6)–C(5)	112.1(9)
O(12)–I(1)–O(11)	99.3(3)	O(23)–I(2)–O(21)	100.3(3)
O(13)–I(1)–O(11)	98.1(3)	O(23)–I(2)–O(22)	94.8(3)
O(13)–I(1)–O(12)	99.5(3)	O(21)–I(2)–O(22)	94.6(4)
O(32)–I(3)–O(33)	97.0(3)	O(1)–C(1)–O(2)	126.0(7)
O(33)–I(3)–O(31)	98.1(3)	O(2)–C(1)–C(2)	111.1(6)
N(8)–C(2)–C(3)	111.2(6)	C(4)–C(3)–C(2)	113.4(7)
N(8)–C(2)–C(1)	107.7(6)	C(5)–C(4)–C(3)	111.4(8)
C(3)–C(2)–C(1)	112.6(7)	C(6)–C(5)–C(4)	116.0(7)

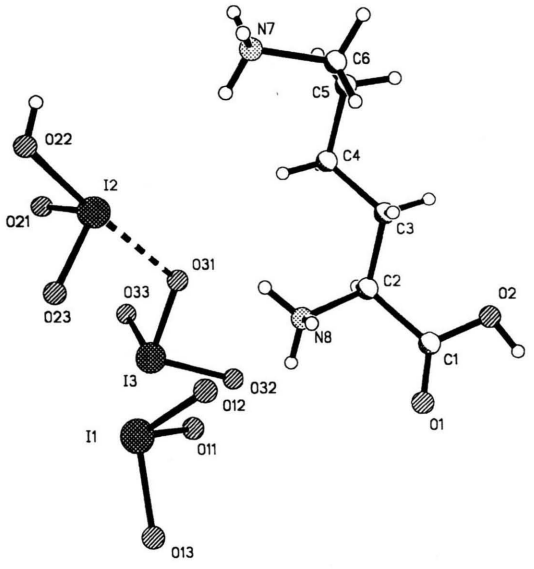

Fig. 4. The asymmetric part of the L-Lys · $3HIO_3$ unit cell.

ble 1). The iodine-127 NQR spectrum consists of three intensive ($S/N > 50$) lines on each transition, resulting from three inequivalent iodine atoms in the unit cell. The asymmetry parameter $\eta = 0.0561$ corresponds to less distorted, $\eta = 0.1240$ to more distorted IO_3 groups, and $\eta = 0.5488$ undoubtedly to the HIO_3 group. The distortion of the IO_3 group can occur from hydrogen bonds and from a strong O...I bond from the second coordination sphere. The high quality Lys · $3HIO_3$ crystals have allowed us to carry out X-ray diffraction, revealing further peculiarities of its structure. 2601 reflections were measured. The crystal is monoclinic with $a = 8.360(2)$ Å, $b = 6.330(1)$ Å, $c = 14.750(3)$ Å, $\beta = 92.86(3)°$, space group $P2_1$, $Z = 2$, $D_c = 2.875$ Mg/m^3. The coordinates of the atoms, appropriate to the final $R_1 = 0.0339$ and $wR_2 = 0.0921$ values, are collected in Table 4, and the bond lengths and angles in Table 5. The asymmetric part of the cell is shown on Figure 4. The hydrogen atoms were not located, and on Fig. 4 they are shown in expected positions based on the bond lengths of the non hydrogen atoms. The C(1)–O(1) and C(1)–O(2) bond lengths indicate the existence of the COOH group in complete accordance with the conclusion made from the IR spectrum. The bond length of I(2)–O(22) indicates that the O(22) atom belongs to a hydroxyl group, and so I(2) to a HIO_3 group. The other two iodine atoms form IO_3 groups which gave their protons for protonation of the two amino groups of lisine. One of them, I(1), forms a less distorted IO_3 group. It is obvious that it is one which has the asymmetry parameter $\eta = 0.0561$. The second atom, I(3), included in a IO_3 group, has in addition to two usual bonds I(3)–O(32) and I(3)–O(33), one lengthened bond I(3)–O(31) which is caused by the strong O(31)...I(2) bond from the second coordination sphere. Such bonds can be considered as intermediate between the first and second coordination spheres [18].

According to [18] it is possible to consider the complex $HI(2)O_3 \cdot I(3)O_3^-$ as a second counter-ion in addition to $I(1)O_3^-$. On the basis of the bond lengths of the $I(3)O_3$ group it was possible to expect a greater asymmetry parameter than $\eta = 0.1240$, however it is necessary to take into account that the X-ray data are taken at room temperature, and the NQR data at the 77 K. Thus, on the basis of the NQR data it is possible to assume that the structure of Lys · $3HIO_3$ at 77 K corresponds well to structural data at room temperature.

Bet · 3HIO$_3$

While Bet · HIO_3 is a poor by crystallizing compound, the interaction of betaine with iodic acid results in well crystallizing Bet · $3HIO_3$. Bet · $3HIO_3$ is formed already at the ratio 1:2 in a water solution. Betaine $(CH_3)_3N^+CH_2COO^-$ is an internal salt, and its interaction with acids results in protonation of the COO^- group. The IR spectrum of Bet · $3HIO_3$ (Fig. 5) contains a band at 1711 cm^{-1} related to the COOH group. The absence of an absorption at 1600 cm^{-1} indicates the absence of COO^- and NH_3^+ groups. The absorption at 635; 675; 716;

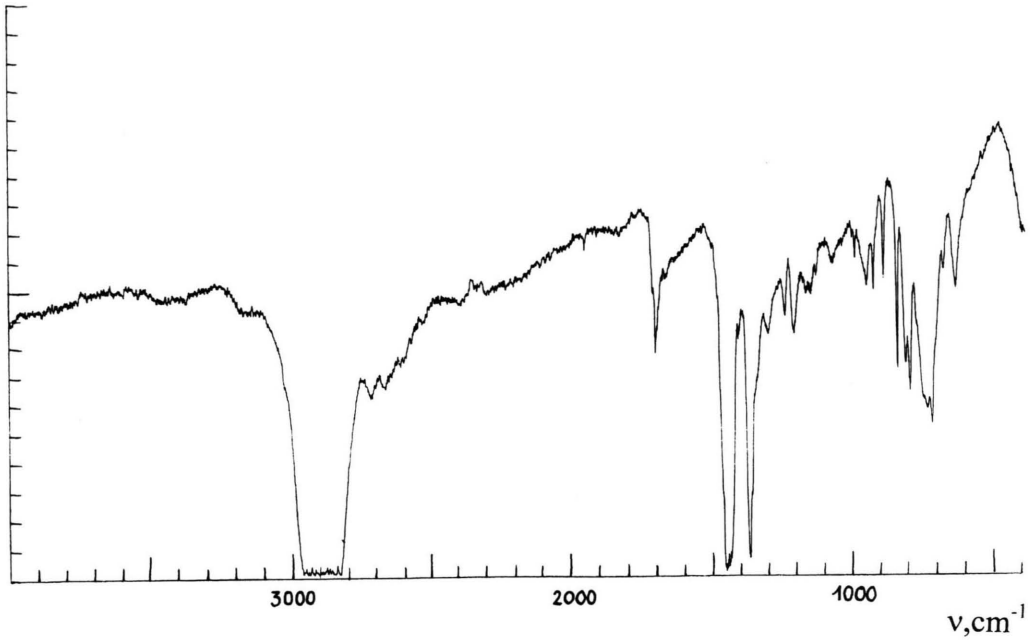

Fig. 5. The IR spectrum of Bet · $3HIO_3$.

Table 6. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å $\times 10^3$] of Bet · $3HIO_3$.

Atom	x	y	z	U(eq)
O(23)	–106(13)	1562(7)	4950(7)	44(2)
I(2)	–2764(1)	926(1)	5356(1)	23(1)
O(22)	–3485(13)	320(7)	4064(5)	36(1)
O(21)	–4397(12)	2585(6)	5385(6)	33(1)
C(5)	–656(19)	4025(9)	8701(10)	42(2)
O(2)	–2373(15)	1542(8)	7613(6)	46(2)
O(1)	–2860(13)	71(8)	9067(6)	40(2)
N(3)	1054(15)	2772(7)	8683(6)	29(2)
C(6)	2145(18)	2618(11)	7537(7)	38(2)
C(2)	31(17)	1436(9)	9085(7)	31(2)
C(1)	–1842(16)	1044(9)	8491(7)	30(2)
C(4)	2724(19)	3017(10)	9443(8)	40(2)
I(3)	–6698(1)	–2453(1)	7620(1)	28(1)
O(32)	–6062(13)	–935(8)	8299(6)	42(2)
O(31)	–6276(18)	–3794(10)	8603(6)	61(2)
I(1)	1853(1)	3663(1)	4377(1)	25(1)
O(33)	–9700(14)	–2092(12)	8061(7)	61(3)
O(13)	–633(13)	4476(7)	3970(5)	36(2)
O(11)	3690(14)	5062(8)	3789(6)	40(2)
O(12)	2686(12)	2586(7)	3202(6)	33(1)

732; 752; 793 and 808 cm^{-1} is connected with stretching vibrations of iodate groups, and the presence of 635 cm^{-1} testifies the existence of the HIO_3 group and, hence, formation of an acid salt of betaine. This conclusion is supported by the NQR data (Table 1). Three inequivalent iodine atoms in the unit-cell formed two HIO_3 groups with $\eta = 0.4451$ and $\eta = 0.4690$ and one rather distorted IO_3 group with $\eta = 0.1934$. Distortions of the IO_3 group can be caused by hydrogen bonds and a strong O...I bond, as in the case of Lys · $3HIO_3$. Further information on the structure of Bet · $3HIO_3$ was obtained from X-ray data. 3692 independent reflections were measured. A triclinic unit cell with parameters $a = 6.228(1)$ Å, $b = 9.481(2)$ Å, $c = 12.252(2)$ Å, $\alpha = 87.98(3)°$, $\beta = 84.47(3)°$, $\gamma = 85.89(3)°$, $Z = 2$, space group $P\bar{1}$, $D_m = 3.06(5)$ Mg/m^3, $D_c = 2.983$ Mg/m^3,was found. The coordinates of atoms for $R_1 = 0.0747$ and $wR_2 = 0.1940$ are collected in Table 6. Bond lengths and angles are listed in Table 7. A fragment of the Bet · $3HIO_3$ structure is shown on Figure 6. The hydrogen atoms have not been located. The bond lengths of C(1)–O(1) and C(1)–O(2) confirm the presence of the carboxyl COOH group, concluded on the basis of the IR spectrum. The bond lengths of I(1)–O(11) and I(3)–O(33) show that these are I–OH bonds, and hence I(1) and I(3) are in HIO_3 groups. The remaining I(2) atom forms an IO_3 group. As in the case of Lys · $3HIO_3$, a short O(23)...I(1) bond is present in the structure of Bet · $3HIO_3$, which results in some lengthening of the I(2)–O(23) bond, and an appropriate increase of asymmetry parameter for a iodate group is also found. There are hydrogen bonds O(1)–H...O(32) (2.538 Å), O(11)–H...O(21A) (2.538 Å) and O(33)–H...O(12A) (2.644 Å).

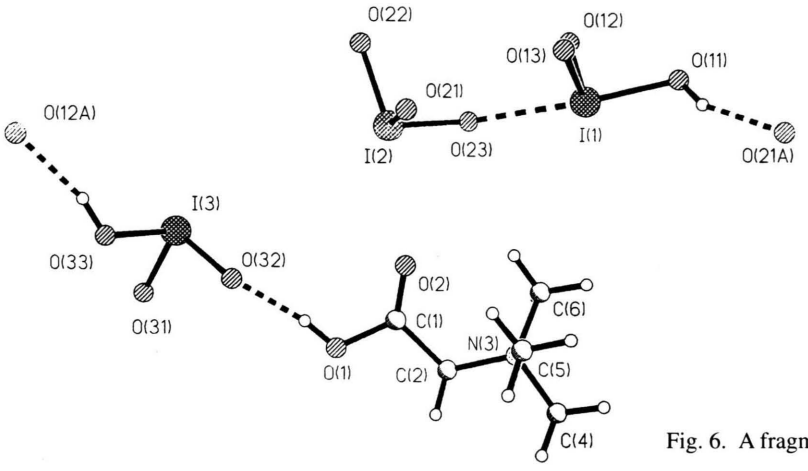

Fig. 6. A fragment of the Bet · $3HIO_3$ structure.

Table 7. Bond lengths [Å] and angles (°) of Bet · $3HIO_3$.

I(1)–O(11)	1.892(7)	O(12)–I(1)–O(11)	89.9(3)
I(1)–O(12)	1.807(6)	O(13)–I(1)–O(12)	100.0(3)
I(1)–O(13)	1.786(7)	O(21)–I(2)–O(22)	97.9(3)
I(2)–O(21)	1.810(6)	O(22)–I(2)–O(23)	101.3(4)
I(2)–O(22)	1.810(6)	O(21)–I(2)–O(23)	100.2(3)
I(2)–O(23)	1.821(8)	O(31)–I(3)–O(32)	102.0(4)
I(3)–O(31)	1.744(8)	O(32)–I(3)–O(33)	91.3(4)
I(3)–O(32)	1.775(7)	O(31)–I(3)–O(33)	95.4(5)
I(3)–O(33)	1.906(9)	O(2)–C(1)–O(1)	124.0(10)
C(1)–O(1)	1.305(11)	O(1)–C(1)–C(2)	109.0(8)
C(1)–O(2)	1.225(11)	O(2)–C(1)–C(2)	126.9(9)
C(1)–C(2)	1.508(14)	C(1)–C(2)–N(3)	115.9(7)
C(2)–N(3)	1.505(11)	C(2)–N(3)–C(4)	106.7(7)
N(3)–C(4)	1.497(13)	C(4)–N(3)–C(6)	108.9(8)
N(3)–C(5)	1.537(12)	C(4)–N(3)–C(5)	110.2(8)
N(3)–C(6)	1.507(11)	C(2)–N(3)–C(6)	111.1(7)
O(23)...I(1)	2.456(7)	C(2)–N(3)–C(6)	110.4(8)
O(23)–I(1)–O(11)	170.1(3)	C(6)–N(3)–C(5)	109.5(8)
O(13)–I(1)–O(11)	97.9(4)		

On Search for Nonlinear Optical Crystals

The role of the various factors in the search for new nonlinear crystals is discussed in [19, 20]. A necessary condition for nonlinear optical properties is the absence of an inversion center in the structure. However, most probable for organic crystals is a symmetry containing an inversion center. Thus, half of the known structures concern 2/m and $\bar{1}$ groups. A guarantee of getting noncentrosymmetric crystals is the use of optically active compounds containing an asymmetric carbon atom, in particular amino acids. Betaine does not contain an asymmetric atom of carbon and thus is not optically active. Thus crystals containing betaine, Bet · $3HIO_3$ and also Bet · H_3PO_4 (results of which will be published elsewhere), belong to the groups with a center of symmetry ($P\bar{1}$ and $P2_1/n$ accordingly). Therefore it is important to use optically active amino acids as, for example, L-arginine and L-lisine, forming the crystals L-Arg · $2HIO_3$ and L-Lys · $3HIO_3$ with symmetry $P2_12_12_1$ and $P2_1$, respectively. Among non centrosymmetric crystals, most (78%) [20] are enantiomorphous crystals. Such crystals have $P2_12_12_1$ or $P2_1$ symmetry. These groups are not equivalent. Preferable is the group $P2_1$. In the crystals with space group $P2_12_12_1$, non critical phase – matching is impossible [21]. Besides, the space group $P2_12_12_1$ admits little (19%) molecular nonlinearity in the macroscopic nonlinearity of a crystal, while space group $P2_1$ admits maximum (38%) contribution [20, 22]. We believe that this can partially explain the difference in the intensities of SHG signals for these groups of symmetry, found by the authors [8].

We also would like to note that the investigation of the L-Arg · $2HIO_3$ crystal structure has shown that it is not an acid iodate and its formation is a peculiarity of arginine, namely presence of two groups which can be protonated. It seems that the formation of Arg · $2HIO_3$ and Arg · $2H_3AsO_4$ [8] is rather a rule than an exception. Thus, the well crystallizing compounds with composition 1:2 grow not only with acids forming poorly crystallizing compounds (e.g. Arg · $2HIO_3$ and Arg · $2HNO_3$) but also with acids forming well crystallizing compounds (e.g. Arg · 2HCl, Arg · $2H_3PO_4$ and others).

So, we agree with the authors of [8] that this class of compounds promises nonlinear crystals with useful properties.

Acknowledgements

The authors thank Dr. A. Aghajanyan for some reagents, Dr. H. Karapetyan for useful discussion and Mr. S. Petrosyan for the help in the preparation of this paper.

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