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Vibrational Spectra, Phase Transition and Nonlinear Optical Properties of Anilinium Perchlorate Molecular-Ionic Solid*

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Crystals of anilinium perchlorate, $C_6H_5NH_3^+ClO_4^-$, were obtained by slow evaporation of an aqueous solution at room temperature. Powder Kurtz-Perry measurements were performed for the title material. The efficiency of second harmonic generation was estimated relative to KDP: $d = 0.21d_{KDP}$. Room temperature powder infrared and Raman measurements for the title solid and its deuterated analogue were carried out. The vibrational spectra in the regions of the internal vibrations of the ions corroborate the X-ray data (reported by Paixão *et al.* [1]). Differential scanning measurements performed on the powder sample indicate a first order phase transition at about 220 K. A possible mechanism of the phase transition is suggested in relation to disorder of the hydrogen atoms on nitrogen atoms (reported in [1]). The role of the aniline molecule in the second harmonic generation is discussed.

Key words: FTIR spectroscopy, FT Raman spectroscopy, hydrogen bonded molecular crystal, phase transitions, second harmonic generation

The association of organic moieties with inorganic residues has been proposed for the preparation of second order nonlinear materials. The organo-mineral crystal 2-amino-5-nitropyridinium dihydrogen monophosphate was studied by Kotler *et al*. [2]. Quasi-perfect polar alignment of nonlinear chromophores in a crystalline H-bonded guest-host structure of 2-amino-5-nitropyridinium-L-monohydrogentartrate was found by Zyss *et al.* [3]. More recently Horiuchi *et al.* [4] measured the second order nonlinear optical coefficient for the organic-inorganic material 2-amino-5-nitropyri-

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* Dedicated to Prof. M. Szafran on the occasion of his 70th birthday.
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dinium chloride. The role of hydrogen bonding was underlined already at an early stage of molecular NLO investigations [5] as well as during successive studies [6–9].

X-ray structural analysis and infrared and Raman spectroscopies can be useful in the clarification of the role of hydrogen bonds in crystals exhibiting non-linear optical properties. There were many important works as to the relation between nonlinear and vibrational properties of molecular systems at the molecular and crystalline levels [10–15].

The aim of the present work was to contribute to the further elaboration of molecular and crystalline guidelines towards optimization of crystals for quadratic nonlinear optics. During our search for hydrogen bonded hybrid (organic-inorganic) materials we became interested in anilinium perchlorate.

Perchloric acid forms interesting complexes with organic cations. There are many examples of perchlorates exhibiting structural phase transitions connected with the ordering of perchlorate anions. Such a phenomenon was observed in solid trimethylammonium perchlorate by Stammler *et al.* [16]. Mylrajan *et al.* [17] studied molecular motions in tetragonal tetramethylammonium perchlorate with the help of vibrational spectroscopy. Pyridinium perchlorate reveals two structural phase transitions at 233 and 345 K, the second one being of the ferroelectric type [18–19]. The P–T phase diagram of this compound was studied by Czarnecki *et al.* [20]. Martin and Pinkerton [21] found that in melaminium diperchlorate hydrate one perchlorate anion is involved in seven or eight hydrogen bonds, depending on the orientation of the disordered water molecules. The other perchlorate anion forms four hydrogen bonds with two different melaminium residues. Differential scanning experiment performed by Drozd *et al.* [22] revealed an interesting sequence of phase transitions. It is very probable that these anomalies are related to the presence in the structure of the disordered unit mentioned above.

Among crystals comprising perchlorate anions, the most interesting for us are those which are non-centrosymmetric because of their non-linear optical properties. Pronounced second harmonic generation was found in L-leucinium perchlorate (SHG efficiency $d = 0.44d_{KDP}$) [23]. This suggests a non-centrosymmetric crystal structure for this compound.

A number of papers devoted to aniline vibrations were already published. The assignments of the vibrational frequencies of deuterated aniline as well as comparison of these frequencies with those of normal aniline were presented by Rai and Maheshwari [24]. The harmonic force field and vibrational spectra of aniline, aniline-NHD and aniline-ND_2 have been calculated *ab initio* by Niu *et al.* [25]. An infrared and Raman vibrational spectroscopic study of metal(II) halide aniline complexes were performed by Akyuz and Davies [26]. Some more specific vibrational studies of aniline derivatives were reported by Ognyanova *et al.* [27], Campagnaro and Wood [28], Derollez *et al.* [29] and Kozhevina *et al.* [30]. It is worthwhile mentioning here the results reported quite recently by Ohashi *et al.* [31]. They found that protonated aniline forms different types of hydrogen bond with neutral aniline: one with the π-electrons of the aromatic ring and the other with the lone pair of the nitrogen

atoms. These results are especially important for the discussion of nonlinear optical properties of aniline-based hydrogen-bonded molecular crystals.

EXPERIMENTAL

The starting compounds, aniline (Aldrich, 99%) and perchloric acid (Merck, 60%) were used as supplied and prepared in the ratio of 1:1. The dissolved acid was added to the hot solution of aniline. The solution remained clear, without any precipitate. Then, the solution was purified with the aid of activated charcoal and slowly evaporated during a few days till crystals appeared. The elemental analysis performed on a Perkin-Elmer 2400 CHN analyzer is consistent with the 1:1 composition of aniline:perchloric acid. Found: C: 37.02%; H: 4.16%; N: 7.29%. Calculated for $C_6H_7N{\times}HClO_4$: C: 37.23%; H: 4.17%; N: 7.24%. The deuterated analogue was obtained by repeated recrystallization from D_2O.

Polycrystalline powders were obtained by grinding in an agate mortar with a pestle. The vibrational measurements were carried out at room temperature. Samples, as suspensions in oil, were put between KBr wafers. The powder infrared spectra were taken in Nujol and Fluorolube emulsions. Infrared spectra were recorded with a Bruker IFS-88 spectrometer in the region 4000–80 cm^{-1} while powder Fourier transform Raman (FT Raman) spectra were taken with the FRA-106 attachment to the Bruker IFS-88 spectrometer equipped with a Ge detector cooled to liquid nitrogen temperature. For the IR spectra the resolution was set at 2 cm^{-1}, signal/noise ratio was established by 32 scans, weak apodisation. For the Raman spectra a Nd:YAG laser of power *ca*. 200 mW was used as an exciting source; the incident laser excitation is 1064 nm. The scattered light was collected at the angle of 180° in the region 3600–80 cm^{-1}, resolution 2 cm^{-1}, 256 scans. Due to the poor detector response, the Raman counterparts of the infrared bands located above 3200 cm^{-1} were not observed in the spectrum.

Differential scanning calorimetry (DSC) was carried out on a Perkin Elmer DSC-7 calorimeter equipped with a CCA-7 low temperature attachment with a heating/cooling rate of 20 K min^{-1}. The sample of mass *ca*. 26 mg was sealed in the aluminium caps.

Second harmonic generation (SHG) experiment was carried out using the Kurtz-Perry powder technique described in [32]. The calibrated samples (the title compound and KDP) were irradiated at 1064 nm by a Nd:YAG laser and the second harmonic beam power diffused by the powder sample (at 532 nm) was measured as a function of the fundamental beam power.

RESULTS AND DISCUSSION

According to [1], anilinium perchlorate crystallizes in the non-centrosymmetric space group $P2_12_12_1$ (No. 19) of the orthorhombic system with $Z = 4$. The hydrogen atoms on the nitrogen are disordered over two sets of positions with occupancies in the ratio 0.54:0.46.

The infrared and Raman spectra for the normal and deuterated anilinium perchlorate are shown in Figs. 1 and 2, respectively. The bands observed in the measured region 4000–80 cm^{-1} arise from the vibrations of protons in the hydrogen bonds and the internal vibrations of anilinium cations and perchlorate anions. The bands below 200 cm^{-1} arise from the lattice vibrations of the crystal. Juxtaposition of the infrared spectrum of anilinium perchlorate crystal with the spectrum of aniline, Fig. 3, shows that many bands corresponding to *e.g.* antisymmetric and symmetric stretching of amino groups disappear in the region 3500–3200 cm^{-1} due to self-association with intermolecular interactions through hydrogen bonds.

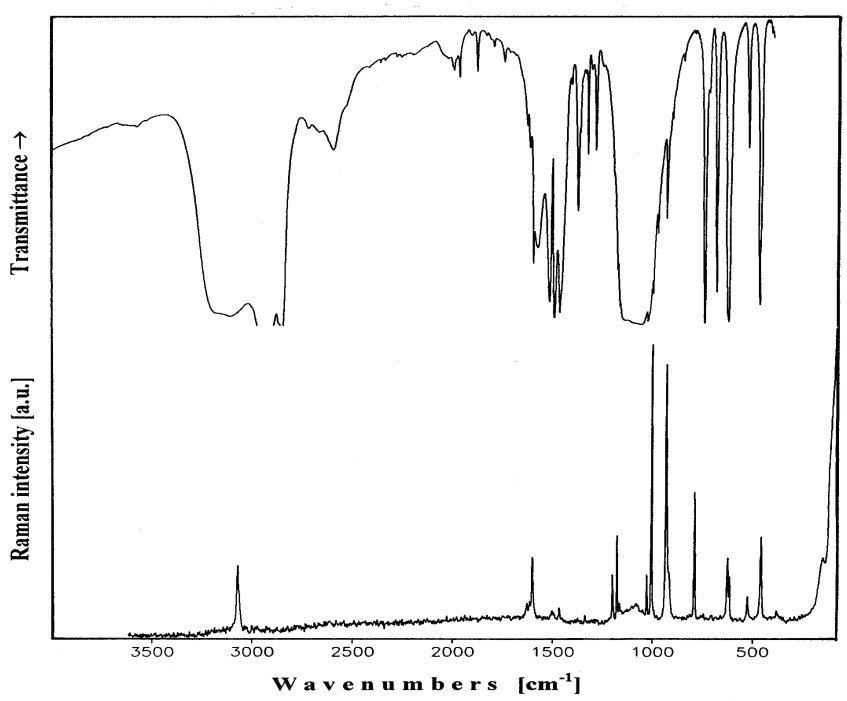

Figure 1. Room temperature powder FTIR and FT Raman spectra of anilinium perchlorate.

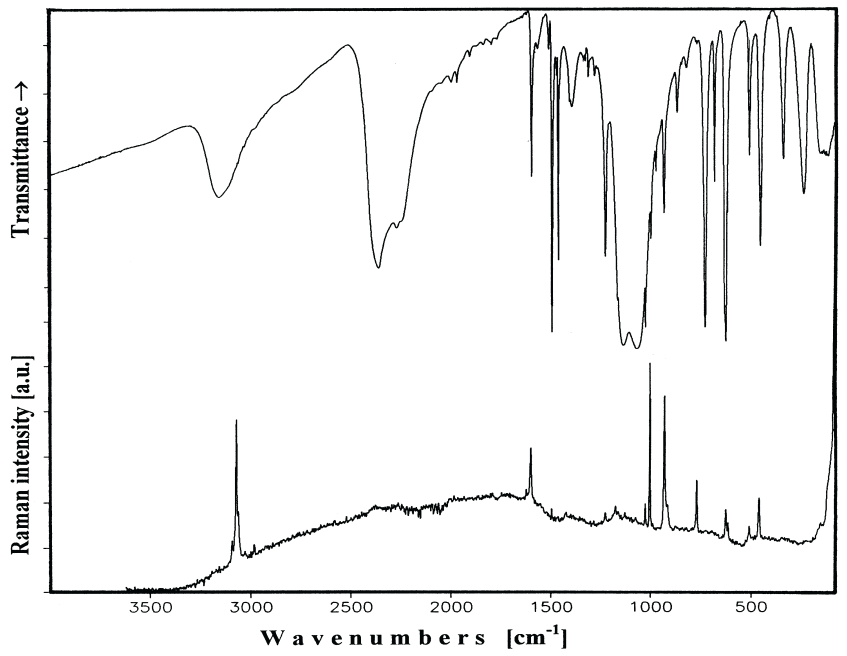

Figure 2. Room temperature powder FTIR and FT Raman spectra of deuterated anilinium perchlorate.

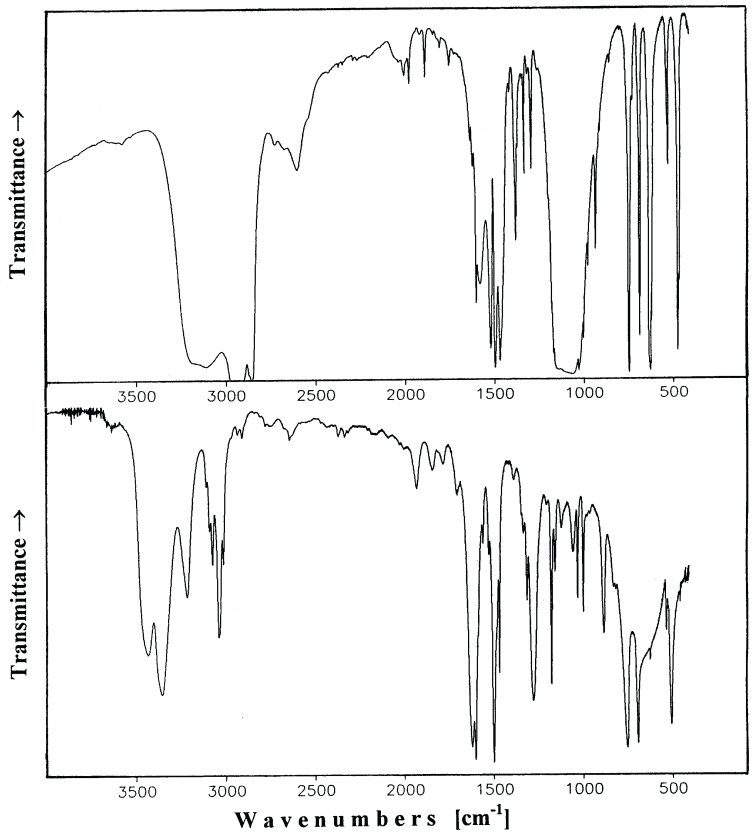

Figure 3. Comparison of room temperature FT IR spectra of anilinium perchlorate (top) and aniline (bottom).

Internal vibrations of the ClO_4^- anion: For an isolated ClO_4 group with T_d symmetry one can expect nine normal modes manifested as four bands in the vibrational spectra ($\nu_1, \nu_2, \nu_3, \nu_4$). According to [33] the frequencies are: $\nu_3(F_2) = 1119$ cm^{-1} (antisymmetric stretching), $\nu_1(A_1) = 928$ cm^{-1} (symmetric stretching), $\nu_4(F_2) = 625$ cm^{-1} (in-plane deformation) and $\nu_2(E) = 459$ cm^{-1} (out-of-plane deformation). The similarity of spectroscopic behaviour between tetrahedral ClO_4^- and SO_4^{2-} anions will be noted below. No band is observed at about 890 cm^{-1} (Cl–O_H stretching, ν'_3). This corroborates the ClO_4^- form of the perchlorate anion with slightly distorted tetrahedral geometry with almost equal Cl–O distances (1.403, 1.425, 1.414 and 1.446 Å, *cf.* [1]). Due to the lowering of the symmetry from the ideal configuration and the crystal field effect, splittings can be observed for the doubly degenerate ν_2 mode and for the triply degenerate ν_3 and ν_4 modes. The assignment of the bands corresponding to particular modes of ClO_4^- anion is given in Table 1.

Table 1. Wavenumbers (cm^{-1}) and relative intensities[a] of the bands observed in the powder infrared and Raman spectra of anilinium perchlorate and its deuterated derivative.

FTIR	FT Raman	FTIR	FT Raman	Assignments
normal		deuterated		
3181 vsb				NH_3^+ asym stretch
3115 vsb				NH_3^+ asym stretch
	3071w	3074m	3071s	νC–H
	3064vwsh	3063m	3062vw	νC–H
		3030m	3027vw	νC–H
		2377sb		ND_3^+ asym stretch (3181/2377 = 1.338)
2984s				
2975s				
		2274m		ND_3^+ asym stretch (3115/2274 = 1.369)
		2253mb		ND_3^+ asym stretch (3115/2253 = 1.381)
2599mb				
2536wsh				
1998vw		1997w		
1970w		1972vw		
1881vw				
1836vw		1841vw		
1798vw		1799vw		
1745vw				
1630w	1627vw	1623vw	1622w	
1617m	1613vw			
1599s	1601w	1598m	1600m	ring stretch
1576sb				NH_3^+ asym def
1518vs				NH_3^+ asym def
1495vs	1502vwb	1497vs	1494w	ring stretch
1467m	1467vw	1464s		ring stretch
1408vw		1408w		
		1395wb		
1328w				N–H···O in-plane def
1288m				N–H···O in-plane def
		1227s	1225w	ND_3^+ asym stretch (1576/1227 = 1.285)
1196m	1200w			N–H···O in-plane def
1178vs	1177w		1171w	N–H···O in-plane def
1166vs	1164vw	1164vs		
1138vsb		1137vsb		ClO_4 asym stretch, ν_3 (F_2)
1100vsb				ClO_4 asym stretch, ν_3 (F_2)
1060vsb		1069vsb		ClO_4 asym stretch, ν_3 (F_2)
1027vs	1028w	1027vs	1025w	
1004vs	1005vs	1004s	1004vs	6(A_1) mode of benzene ring

Table 1 (continuation)

1000vs		1000s		ring C=C sym stretch
978ssh		978msh		
975s		975m		
933s	932vs	933m	932vs	ClO_4 sym stretch, ν_1 (A_1)
918msh	919w	918w	917w	C–C and C–N stretch
		870w		N–D···O in-plane def (1196/870 = 1.375)
849vw		849vw		
		825vw		N–D···O in-plane def (1178/825 = 1.428)
791vw	791m	773vw	771m	in-plane ring def
744vs		727vs		in-plane ring def
688s				
684vs		681m		in-plane ring def
630vssh		630vssh		ClO_4 asym def, ν_4 (F_2)
625vs	627w	625vs	627w	ClO_4 asym def, ν_4 (F_2)
617vs	617w	616m	615w	ClO_4 asym def, ν_4 (F_2)
527m	527vw	509w	509w	ClO_4 sym def, ν_2 (E)
470vs		454s		ClO_4 sym def, ν_2 (E)
380m	382vw	341m		
262s		240m		
159m	149w	156m	153w	
110w	92vssh	116m	118msh	

[a]Abbreviations: s – strong, w – weak, v – very, sh – shoulder, b – broad, m – medium.

One can expect bands from the ν_3 vibration at about 1100 cm^{-1}. Thus, the bands observed only in the infrared spectrum as very strong and broad absorptions at 1138, 1100 and 1060 cm^{-1} were attributed to this mode. According to [34] such a spectroscopic behaviour corresponds to the expected one. In the infrared spectrum of sulphates containing SO_4^{2-} anions [35–37] one can notice very strong bands at about 1200 cm^{-1}, which unambiguously originate from antisymmetric stretching vibrations. It seemed worthwhile noticing that in the case of the $K_4LiH_3(SO_4)_4$ [38] crystal similar bands are observed in the infrared spectrum at 1227 and 1176 cm^{-1}. For $Rb_4LiH_3(SO_4)_4$ [39] they are observed at 1227 and 1198 cm^{-1}.

The ν_1 band is observed at 932 cm^{-1} as very strong and strong in the Raman and infrared spectrum, respectively. Similar bands are observed at 1026, 1015 and 1002 cm^{-1} in crystalline complex of L-lysine with sulphuric acid [23] as well as at 1051 and 1052 cm^{-1} for $K_4LiH_3(SO_4)_4$ and $Rb_4LiH_3(SO_4)_4$, respectively. The ν_4 bands at 630, 625 and 617 cm^{-1} are very strong in the infrared spectrum, while ν_2 bands at 527 and 467 cm^{-1} are strong in the infrared and weak in the Raman spectrum.

The vibrations of the anilinium cation: Most bands observed in infrared and Raman spectra of the title compound belong to benzene ring modes, only some of them may be assigned to the NH_3^+ group. For the assignment of phenyl ring modes the

classical work of Herzberg [40] as well as paper by Miller [41] are helpful. Herzberg's notation was used for numbering normal modes associated with the phenyl ring. Two very strong infrared bands at 1004 and 1000 cm^{-1} form a doublet with very strong Raman counterpart at 1005 cm^{-1}. These bands were attributed to the $6(A_1)$ mode of the benzene ring. The observed splitting may correspond to crystal field effect, as there are four crystallographically equivalent ions in the elementary unit cell [1]. The position of these characteristic bands do not change upon deuteration, and for the deuterated analogue strong and very strong bands are observed at 1004 cm^{-1} in the infrared and Raman spectrum, respectively. The in-plane ring deformation, $8(B_1)$, gives the infrared bands at 744, 684 and 630 cm^{-1}. Other reliable group vibrations of the benzene ring are the stretching ones [42]. The very strong infrared bands at 1518 cm^{-1}, as well as the medium band at 1467 cm^{-1}, were attributed to ring stretching vibrations. For other assignment of internal vibrations of the anilinium cation see Table 1.

The vibrations of the hydrogen bonds: According to the crystal data [1] two sets of positions for hydrogen atoms of protonated amino group could be realised: {H1A, H1B, H1C} with occupation factor equal to 0.54, and {H1D, H1E, H1F} with occupancy factor equal to 0.46. Taking into account these two possibilities, the hydrogen bonds formed are summarized in Table 2. Except for one N–H···Cl hydrogen bond, all the N–H···O hydrogen bonds cover the range 2.835–3.279 Å with an average value of 3.019 Å. The vibrations of these bonds manifest themselves as perturbed NH_3^+ group vibrations. All three protons of this group are engaged in weak interactions as mentioned above. A broad and intense absorption observed in the range 3800–2700 cm^{-1} was assigned to antisymmetric and symmetric stretching vibrations of NH_3^+ group interacting through hydrogen bonds with oxygens of perchlorate anions. There are several bands in the infrared spectrum, which vanish upon deuteration (1576sb, 1518vs, 1328w, 1288m, 1196m, 1166vs) and thus may originate from in-plane deformations of hydrogen bonds. Their Raman counterparts are very weak or not visible. Some new bands, *i.e.* 1227s, 870w, 825vw are observed in the infrared spectrum of the deuterated analogue. The very strong infrared band at 744 cm^{-1} assigned to the in-plane ring deformations moved upon deuteration to 727 cm^{-1}. Similarly the medium Raman band at 791 cm^{-1} moved to 771 cm^{-1}. It is worthwhile to mention that many bands exhibit upon deuteration a pronounced shift towards lower wavenumbers, *e.g.* medium bands at 380 and 260 cm^{-1} move to 341 and 240 cm^{-1}, respectively.

Table 2. Hydrogen-bonding geometries (Å, deg.) for anilinium perchlorate, according to data taken from ref. [1].

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	angle D–H···A (deg.)
N–H(1A)···O2′	0.839	2.523	3.109	127.8
N–H(1A)···O4′	0.839	2.394	3.030	133.0
N–H(1A)···O3′	0.839	2.572	3.111	123.1
N–H(1B)···O2′	0.836	2.367	2.976	130.2
N–H(1B)···O4′	0.836	2.388	3.015	132.3
N–H(1C)···O1′	0.841	2.041	2.835	157.0
N–H(1D)···O1′	0.840	2.550	2.835	101.2
N–H(1D)···O2′	0.840	2.446	2.976	121.9

Table 2 (continuation)

N–H(1D)···O3′	0.840	2.462	3.279	164.4
N–H(1E)···O1′	0.841	2.518	2.835	103.5
N–H(1E)···O3′	0.841	2.304	3.111	160.9
N–H(1E)···O4′	0.841	2.540	3.030	118.2
N–H(1F)···Cl′	0.841	2.841	3.669	168.3
N–H(1F)···O2′	0.841	2.354	3.109	149.7
N–H(1F)···O4′	0.841	2.293	3.015	144.1

′Denotes atoms generated with symmetry codes.

Phase transition: Differential scanning calorimetry measurements indicate a phase transition of the first order at *ca.* 224 and 221 K for heating and cooling, respectively, see Fig. 4. This effect is accompanied by an enthalpy change ΔH equal to *ca.* 0.39 J g^{-1}. An additional anomaly at *ca*. 215 K with ΔH = 0.037 J g^{-1} was observed during heating of the sample.

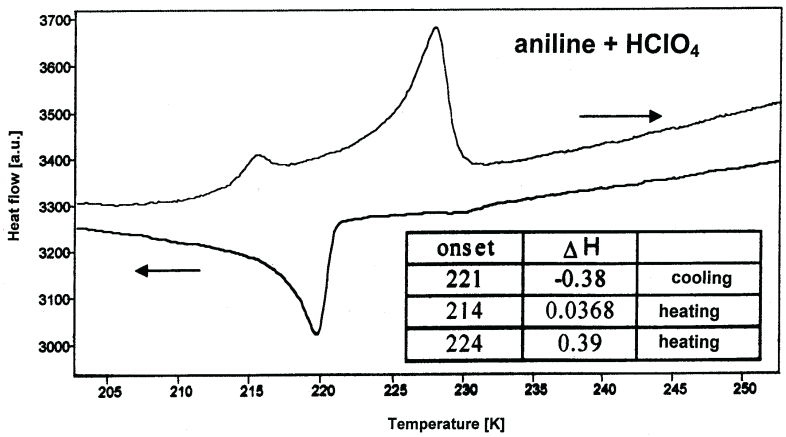

Figure 4. DSC diagram for anilinium perchlorate.

The results mentioned above correspond to the fact that the hydrogen atoms on the nitrogen are disordered over two sets of positions [1] and like in other complex of p-nitroanilinium perchlorate crystal [43] the hydrogen bonds formed between the NH_3^+ group of anilinium cations and the oxygens of the perchlorate anion are relatively weak. The broad and intense Rayleigh wing observed in the Raman spectrum may reflect this disorder. In such a case the observed calorimetric effect can be explained by the kind of ordering of protons. To confirm such an assumption further investigations like low temperature vibrational measurements are in progress.

Second harmonic generation: For the powder SHG efficiency of the crystal presented here we have obtained the following value relative to KDP: $d_{eff} = 0.2 d_{KDP}$. The quadratic dependence of the second harmonic green light intensity ($I_{2\omega}$) on the intensity of infrared exciting beam (I_{ω}) for anilinium perchlorate polycrystalline sample is shown in Fig. 5.

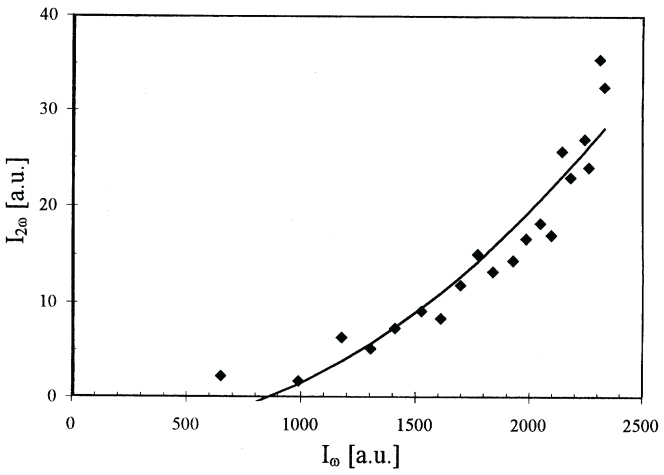

Figure 5. The quadratic dependence of the second harmonic green light intensity ($I_{2\omega}$) on the intensity of infrared exciting beam (I_{ω}) for anilinium perchlorate polycrystalline sample.

The behaviour of aniline molecule in nonlinear optical processes of second and third order was discussed by Nalwa, Watanabe and Miyata [44] and Nalwa [45], respectively. The molecular polarizabilities are defined by the dipole moment P, induced by the electric field E, in which it is immersed, $P = P^0 + \alpha \cdot E + \frac{1}{2}\beta:EE + \ldots$, where linear polarizability α is a matrix and hyperpolarizability β is a 3rd rank tensor. Hyperpolarizability data for aniline obtained by the electric-field-induced second harmonic (EFISH) technique (also known as dc SHG technique) were provided by Nicoud and Twieg [46]. In the benzene molecule, quadratic polarizability disappears due to symmetry with the center of inversion. For conjugated molecules β arises from the distortion of the π-electron distribution caused by substituent group [47]. The aniline molecule consist of a benzene ring, in which an electron donor amino (NH_2) group is substituted. This substitution removes such a restriction and thus generates β. In the title crystal the intermolecular interactions of the anilinium cation with the inorganic part, *i.e.* perchlorate anion leads to a non-centrosymmetric crystal architecture and the inherent properties of the aniline molecule are conserved on the macroscopic scale. In spite of limitations due to the crystal structure (see *e.g.* [48]) the studied crystal provides additional arguments in the discussion of the role of hydrogen bonds in the self-assembly phenomenon giving non-centrosymmetric crystals with potential applications in nonlinear optics.

CONCLUSIONS

The vibrational spectra of title crystal support structural data reported by Paixão *et al.* [1]. Similarly to other aniline-based crystalline ionic complexes like anilinium trichloroacetate, anilinium tartrate, anilinium nitrate and anilinium p-toluenesulfonate [23], anilinium perchlorate exhibits second order nonlinear optical properties.

The SHG efficiency of this crystal was estimated as $0.2d_{KDP}$. Differential scanning calorimetry measurements indicate clearly a first order phase transition at *ca.* 220 K. This anomaly may be related to the fact, that the hydrogen atoms on the nitrogen are disordered over two sets of positions.

Acknowledgments

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REFERENCES

1. Paixão J.A., Matos Beja A., Ramos Silva M., Alte da Veiga L. and Martin-Gil J., *Z. Kristallogr. NCS*, **214**, 85 (1999).
2. Kotler Z., Hierle R., Josse D., Zyss J. and Masse R., *J. Opt. Soc. Am. B – Opt. Phys*., **9**, 534 (1992).
3. Zyss J., Masse R., Bagieu-Beucher M. and Levy J.P., *Adv. Mater*., **5**, 120 (1993).
4. Horiuchi N., Lefaucheux F., Ibanez A. and Zyss J., *J. Opt. Soc. Am. B – Opt. Phys*., **19**, 1830 (2002).
5. Zyss J., Nicoud J.F. and Coquillay M., *J. Chem. Phys*., **81**, 4160 (1984).
6. Ledoux I., Zyss J., Siegel J.S., Brienne J. and Lehn J.-M., *Chem. Phys. Lett*., **172**, 440 (1990).
7. Thalladi V.R., Brasselet S., Weiss H.-Ch., Bläser D., Katz A.K., Carrell H.L., Boese R., Zyss J., Nangia A. and Desiraju G.R., *J. Am. Chem. Soc*., **120**, 2563 (1998).
8. Zyss J., Brasselet S., Thalladi V.R. and Desiraju G.R., *J. Chem. Phys*., **109**, 658 (1998).
9. Thalladi V.R., Boese R., Brasselet S., Ledoux I., Zyss J., Jetti R.K.R. and Desiraju G.R., *Chem. Commun.*, 1639 (1999).
10. Del Zoppo M., Castiglioni C., Tommasini M., Mondini P. and Zerbi G., *Synthetic Metals*, **102**, 1582 (1999).
11. Rumi M. and Zerbi G., *J. Mol. Struct*., **509**, 11 (1999).
12. Del Zoppo M., Castiglioni C., Zuliani P., Razelli A., Tommasini M., Zerbi G. and Blanchard-Desce M., *J. Appl. Polymer Sci.*, **70**, 1311 (1998).
13. Rumi M., Zerbi G. and Mullen K., *J. Chem. Phys*., **108**, 8662 (1998).
14. Quinet O. and Champagne B., *J. Chem. Phys.*, **115**, 6293 (2001).
15. Quinet O. and Champagne B., *Int. J. Quantum Chem*., **89**, 341 (2002).
16. Stammler M., Bruenner R., Schmidt W. and Orcutt D., *Adv. X-Ray Anal*., **9**, 170 (1966).
17. Mylrajan M. and Srinivasan T.K.K., *J. Raman Spectrosc*., **22**, 53 (1991).
18. Czarnecki P., Nawrocik W., Pająk Z. and Wąsicki J., *Phys. Rev*., **B49**, 1511 (1994).
19. Czarnecki P., Nawrocik W., Pająk Z. and Wąsicki J., *J. Phys. Cond. Matter*, **6**, 4955 (1994).
20. Czarnecki P., Wąsicki J., Pająk Z., Goc R., Małuszyńska H. and Habryło S., *J. Mol. Struct*., **404**, 175 (1997).
21. Martin A. and Pinkerton A.A., *Acta Cryst*., **C51**, 2174 (1995).
22. Drozd M. and Marchewka M.K., unpublished results.
23. Marchewka M.K. and Ratajczak H., unpublished results.
24. Rai J.N. and Maheshwari R.C., *Current Science*, **39**, 435 (1970).
25. Niu Z., Dunn K.M. and Boggs J.E., *Mol. Phys*., **55**, 421 (1985).
26. Akyuz S. and Davies J.E.D., *J. Mol. Struct*., **95**, 157 (1982).
27. Ognyanova V., Andreev G.N., Stamboliyska B. and Juchnovski I.N., *J. Mol. Struct*., **513**, 139 (1999).
28. Campagnaro G.E. and Wood J.L., *J. Mol. Struct*., **6**, 117 (1970).
29. Derollez P., Bee M. and Jobic H., *Spectrochim. Acta*, **48A**, 743 (1992).
30. Kozhevina L.I., Prokopenko E.B., Rybachenko V.I. and Titov E.V., *Zh. Prikl. Spektr.*, **60**, 19 (1994).
31. Ohashi K., Inokuchi Y., Izutsu H., Hino K., Yamamoto N., Nishi N. and Sekiya H., *Chem. Phys. Lett*., **323**, 43 (2000).
32. Kurtz S.K. and Perry T.T., *J. Appl. Phys*., **39**, 3798 (1968).
33. Siebert H., *Z. Anorg. allg. Chem*., **275**, 225 (1954).

34. Nakamoto K., *Infrared and Raman Spectra of Inorganic and Coordination Compounds*,Wiley, NY, 1986.
35. Schulze H., Weinstock N., Mueller A. and Vandrish G., *Spectrochim. Acta*, **29A**, 1705 (1973).
36. Videnova-Adrabińska V., *J. Mol. Struct*., **237**, 367 (1990).
37. Damak M., Kamoun M., Daoud A., Romain F., Lautie A. and Novak A.,*J. Mol. Struct*., **130**, 245 (1985).
38. Marchewka M.K., Baran J. and Ratajczak H., *Vibr. Spectr.*, accepted (2003).
39. Baran J., Marchewka M.K., Ratajczak H. and Czapla Z., *J. Mol. Struct*., **436–437**, 281 (1997).
40. Herzberg G., *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand, NY, 1945.
41. Miller F.A., *J. Raman Spectrosc*., **19**, 219 (1988).
42. Brownlee R.T.C., Cameron D.G., Topsom R.D., Katrizky A.R. and Sparrow A.J.,*J. Mol. Struct*., **16**, 365 (1973).
43. Marchewka M.K., Drozd M. and Pietraszko A., *Mat. Sci. Eng. B*, **B100**, 225 (2003).
44. Nalwa H.S., Watanabe T. and Miyata S., *Nonlinear Optics of Organic Molecules and Polymers*, Nalwa H.S., Miyata S., Eds., CRC Press, 1997, pp. 97–98.
45. Nalwa H.S., *Nonlinear Optics of Organic Molecules and Polymers*, Nalwa H.S. and Miyata S., Eds., CRC Press, 1997, p. 623.
46. Nicoud J.F. and Twieg R.J., *Nonlinear Optical Properties of Organic Molecules and Crystals*, Chemla D.S., Zyss J., Eds., Academic Press, London, 1987, Vol. 2, p. 257.
47. Zyss J. and Chemla D.S., *Nonlinear Optical Properties of Organic Molecules and Crystals*, Chemla D.S., Zyss J., Eds., Academic Press, London, 1987, Vol. 1, pp. 73–74.
48. Bosshard Ch., Sutter K., Prętre Ph., Hullinger J., Flörsheimer M., Kaatz P. and Günter P., *Organic Nonlinear Optical Materials*, Gordon and Breach Publishers, 1995, pp. 37–39.