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Enhancement of the electro-optic properties in hybrid organic–inorganic crystals by molecular engineering

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The electro-optic properties and their frequency dispersion of the 2-amino-5-nitropyridium monohydrogen L-tartrate (2A5NPLT) are investigated at room temperature at a wavelength of 632.8 nm. The results show a large increase (more than three times higher) of the electro-optic coefficient values in the 2A5NPLT crystal compared with the 2A5NPDP crystal, which is one of the first crystals engineered with the 2-amino-5-nitropyridine highly polarizable chromophore.

1. INTRODUCTION

In the past two decades, extensive research has shown that organic crystals can exhibit nonlinear and thus electro-optic (EO) properties that are comparable with or even better than those of the best inorganic materials.^{1,2} This is due to highly polarizable molecules that involve a conjugated system of π electrons such as polyenes or aromatic compounds. Nevertheless, because of their poor chemical stability and low thermal and mechanical resistance, the use of organic molecular crystals is currently limited in their industrial application.

To overcome these difficulties, a strategy has been developed that aims to build cohesive acentric crystalline structures based on host–guest chemistry.³ The attachment of highly polarizable organic cations onto various anionic matrices leads to short and three-dimensional (3-D) networks of short hydrogen bonds. Several polarizable molecules were selected in this crystal engineering and particularly 2-amino-5-nitropyridine (2A5NP). A great number of hydrogen bond salts having a 3-D acentric structure based on polar herringbone motifs were obtained with this push–pull molecule such as dihydrogen phosphate⁴ or dihydrogen arsenate.⁵ These salts possess enhanced stability (chemical, thermal, mechanical) compared with corresponding molecular organic crystals. Moreover, they exhibit a wider transparency range and bulky crystal morphology.^{6,7}

Unfortunately, as shown recently,^{8,9} the EO properties of the first two compounds did not reach our expectation. Indeed, the larger value of the effective EO coefficient that we measured in the 2-amino-5-nitropyridine dihydrogen phosphate (2A5NPDP) crystal was equal to 11 pm/V. This value is of the same order of magnitude as

that of the inorganic KDP family type.¹⁰ As has been shown in Refs. 8 and 9, the EO properties of the hybrid organic–inorganic crystals can be attributed mainly to organic cations (the contribution of the inorganic subnetwork to the EO coefficient can be neglected). Thus, we believe that the low EO coefficient value for these crystals arises from the misalignment between the charge transfer axis of the organic chromophores in the crystal and the light polarization direction. Indeed, the herringbone motif, which is favorable to second-harmonic generation, corresponds to a quite significant misalignment angle (35 deg in the case of 2A5NPDP crystal) and thus yields to low EO properties.

From the crystal engineering mentioned above, a new type of hydrogen bond salt structure was discovered.^{11,12} This new material, 2-amino-5-nitropyridinium monohydrogen L-tartrate (2A5NPLT), was shown to have 2A5NP⁺ cations nearly aligned with the crystallographic b axis (see Fig. 1). In the following we propose to characterize the EO properties of this compound to check if this quite good alignment of the dipole moments yields an enhancement of the EO properties.

2. PREPARATION OF 2A5NPLT CRYSTAL AND SAMPLE

High-purity 2A5NPLT salt was synthesized from the dissolution of purified 2A5NP (multiple sublimation) and L-Tartaric acid in hot acetic acid aqueous solution (14 M). Crystals were grown from solution both by the standard temperature-lowering method¹³ and a rapid growth technique derived from the one developed for KH_2PO_4 .^{14,15} With the latter technique, we obtained single crystals,

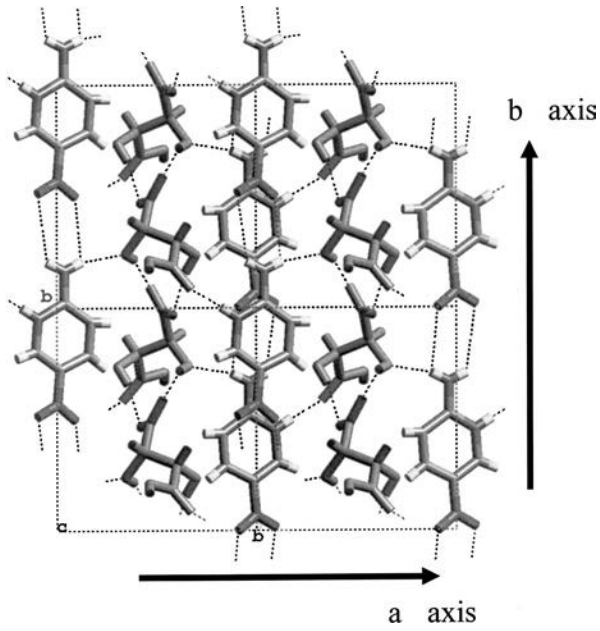


Fig. 1. Projection of the polar structure of 2A5NPLT in the ab plane showing a quasi-perfect alignment of the 2-amino-5-nitropyridium cations.

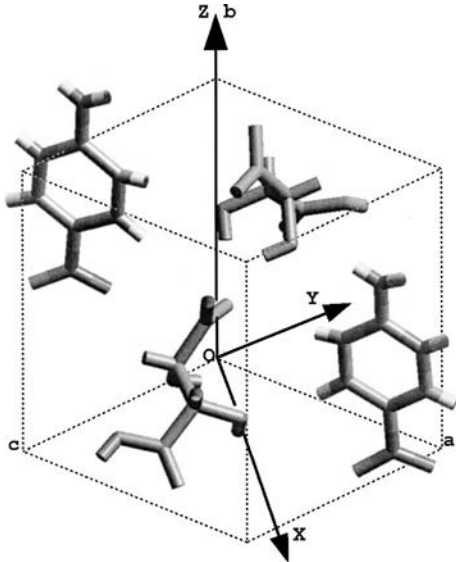


Fig. 2. Orientation of dielectric and crystallographic axes with respect to each other in 2A5NPLT crystals. The dielectric X axis is in the (ac) plane at 56° from the crystallographic c axis and the Y axis lies in the $2A5NP^+$ molecular plane.

several millimeters in size (typically $5 \text{ mm} \times 5 \text{ mm} \times 10 \text{ mm}$), in approximately 3 weeks. The quality of these crystals was controlled by x-ray diffraction topography. The arrangement of the optically active molecule in the structure is highly polar, the charge transfer axis of the $2A5NP^+$ cation being almost aligned (3.6°) with the dielectric Z axis (corresponding to the crystallographic b axis, as seen in Fig. 2). According to Ref. 11, the dielectric X axis is in the (ac) plane at 56° from the crystallographic c axis and the Y axis lies in the $2A5NP^+$ molecular plane. As the 2A5NPLT crystals belongs to the $P2_1$ symmetry group, where the twofold axis is along the prin-

cipal dielectric Z axis, the linear EO properties of this crystal are described in abbreviated notation by eight coefficients, r_{13} , r_{23} , r_{33} , r_{63} , r_{42} , r_{52} , r_{41} , and r_{51} . Here we focus our attention only on coefficients r_{13} , r_{23} , and r_{33} for which the contribution of the organic molecule to the EO properties is the largest.⁹ If the light beam propagates along the principal X axis, the principal Y axis or the Z axis and the electrical field is applied along the Z axis, the field-induced birefringences in (Y, Z) , (X, Z) , and (X, Y) planes are given, respectively, by

$$\begin{aligned} \Delta n_{yz}(E) &= -\frac{n_2^3 r_a E_z}{2}, & \Delta n_{xz}(E) &= -\frac{n_1^3 r_b E_z}{2}, \\ \Delta n_{xy}(E) &= -\frac{n_1^3 r_c E_z}{2}, \end{aligned} \quad (1)$$

where the effective coefficients r_a , r_b , and r_c are defined by

$$\begin{aligned} r_a &= r_{23} - \frac{n_3^3}{n_2^3} r_{33}, & r_b &= r_{13} - \frac{n_3^3}{n_1^3} r_{33}, \\ r_c &= r_{13} - \frac{n_2^3}{n_1^3} r_{23}. \end{aligned} \quad (2)$$

Finally, the field-induced phase shift between the two components of the light polarization can be expressed by

$$\Gamma(E) = \frac{2\pi L}{\lambda} \Delta n(E), \quad (3)$$

where L is the crystal length along the light propagation direction, λ is the wavelength of the light beam, and $\Delta n(E)$ is the field-induced birefringence in the light path.

Only one sample is necessary for the measurement of EO coefficients r_a , r_b , and r_c . The sample was prepared as a parallelepiped with the principal axes X , Y , and Z perpendicular to the faces. The six faces were optically polished. Gold electrodes were evaporated on the Z faces (electric field should be applied along the Z axis) taking care to let a small surface free of gold (see Fig. 3) to allow

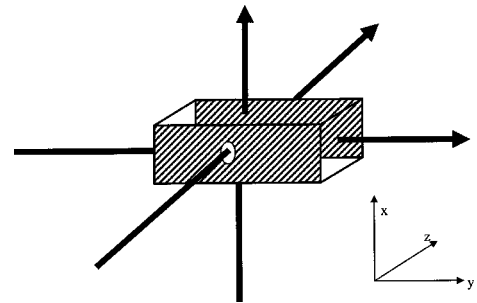


Fig. 3. Schema of the prepared sample used for the EO characterization of the 2A5NPLT crystals. Gold electrodes were deposited on z faces taking care to let a small surface free of gold to allow the light beam to go through the sample in the Z direction. This sample allows the measurement of the EO coefficient r_a , r_b , and r_c for a light beam that propagates along the X , Y , and Z directions, respectively, and for an applied electric field along the Z axis.

the light beam to go through the sample in the Z direction and thus to have the possibility to measure the EO coefficient r_c .

3. EXPERIMENTAL SETUP AND TECHNIQUE

To determine the EO coefficients r_a and r_b and their frequency dependence, we used the time response method (TRM)^{16,17} with the Sénarmont setup, which allows us to obtain the clamped (r^S) and unclamped (r^T) EO coefficients corresponding, respectively, to the measured coefficients at short (or high-frequency) and long (or low-frequency) periods of time. The difference between the values of r^T and r^S gives the acoustic contribution to the EO coefficient. This contribution arises from indirect modulation of the susceptibility by means of crystal deformations¹⁸ and can be written as

$$r_{ijk}^T - r_{ijk}^S = \sum_{m,n} p_{ijmn} d_{mnk}, \quad (4)$$

where p_{ijmn} and d_{mnk} are the components of the elasto-optic and piezoelectric tensor, respectively.

The method that we used consists in the measurement of the time response of the EO crystal to a voltage step. We obtained the latter by switching a large voltage (up to 1 kV) in a short period of time (a few nanoseconds). At the point of the transmittance curve of the Sénarmont setup corresponding to the maximum of modulation intensity, the time dependence of the variation of the transmitted beam intensity $\Delta i(t)$ induced by the applied voltage $\Delta V(t)$ yields the time response of the EO crystal under test as

$$\Delta i(t) = \frac{\pi n_{\text{eff}}^3 L I_0}{2\lambda d} r_{\text{eff}}(t) \otimes \Delta V(t), \quad (5)$$

where \otimes is the convolution operator and $r_{\text{eff}}(t)$ is the actual value of the EO coefficient. $I_0 = I_{\text{max}} - I_{\text{min}}$ represents the total intensity range of the transfer function and d is the interelectrode spacing. From the measurement of $\Delta i(t)$ and $\Delta V(t)$, the frequency dispersion of the EO coefficients can be derived from the ratio of $\Delta i(\nu)$ and $\Delta V(\nu)$ which were obtained by the Z transform of signals $\Delta i(t)$ and $\Delta V(t)$, respectively¹⁵:

$$r_{\text{eff}}(\nu) = \frac{2\lambda d}{\pi n_{\text{eff}}^3 I_0 L} \frac{\Delta i(\nu)}{\Delta V(\nu)}. \quad (6)$$

We also determined the coefficient r_c using the Sénarmont setup by means of the ac modulation method.¹⁹ Within the TRM, the efficiency of the EO effect in this configuration [the ratio L/d in Eq. (5) is equal to 1 in this case, leading to a weak induced phase shift Γ] was indeed not enough to reach a good signal-to-noise ratio.

We have measured the time response and determined the frequency dispersion of the r_a and r_b coefficients. We also measured the value of the r_c coefficient for frequencies of the applied electric field that vary between 1 and 10 kHz. We obtained all these data using the 632.8-nm wavelength of a He-Ne laser. The amplitudes of the ap-

plied voltage that we used were in the 250–500-V range. The dimensions of the sample were $X \times Y \times Z = 5 \text{ mm} \times 5 \text{ mm} \times 1.1 \text{ mm}$.

4. RESULTS AND DISCUSSION

As an example, Fig. 4 displays a typical record of applied voltage and corresponding induced optical intensity variation versus time obtained during EO measurements when we used the TRM. It corresponds to the case of the r_a coefficient. In the long-time range the optical signal oscillates with a period that corresponds to the main piezoelectric frequency resonance.¹⁶ The oscillations of the optical signal tend to vanish for a time longer than several tens of microseconds. It is to be noted that these oscillations do not exist in the short-time regime ($<100 \text{ ns}$) since acoustic waves need more time to go through the crystal. In this time range the optical response is flat (see the inset in Fig. 4). The relatively weak amplitude of the oscillations and the relatively small difference between the value of the optical signal at long and short times indicate that the acoustic contribution to the EO effect in this material is not strong.

The frequency dispersion of the EO coefficient r_a can be derived, according to Eq. (6), from the ratio of $\Delta i(\nu)$ and $\Delta V(\nu)$, which were obtained by the Z transform of the $\Delta i(t)$ and $\Delta V(t)$ signals shown in Fig. 4. This mathematical treatment was carried out for both EO coefficients r_a and r_b , and the results are plotted in Fig. 5. The frequency varies in the range from 10 kHz to 200 MHz, limited in the low-frequency part by the duration of the voltage pulse and in the high-frequency part by the rise time of the voltage step. On both sides of the acoustic resonances, the dispersion of the EO coefficients r_a and r_b is flat and the corresponding value of each plateau allows us to determine the unclamped (low-frequency) and clamped (high-frequency) values of the coefficients.

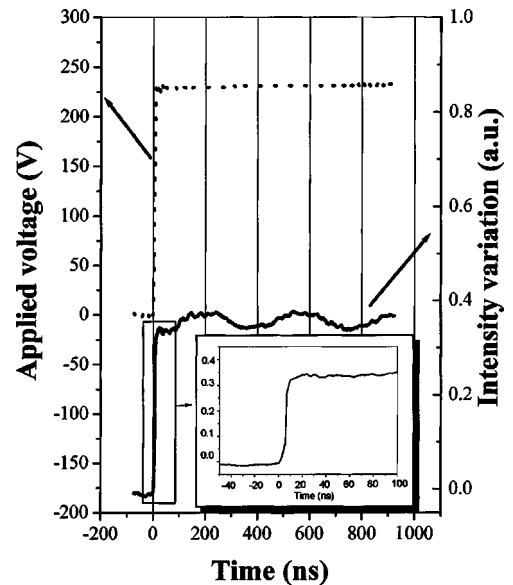


Fig. 4. Typical record of applied voltage (left part) and corresponding induced intensity variation (right part) versus time obtained during EO measurements when we used the TRM, corresponding to the case of coefficient r_a in the 2A5NPLT crystal.

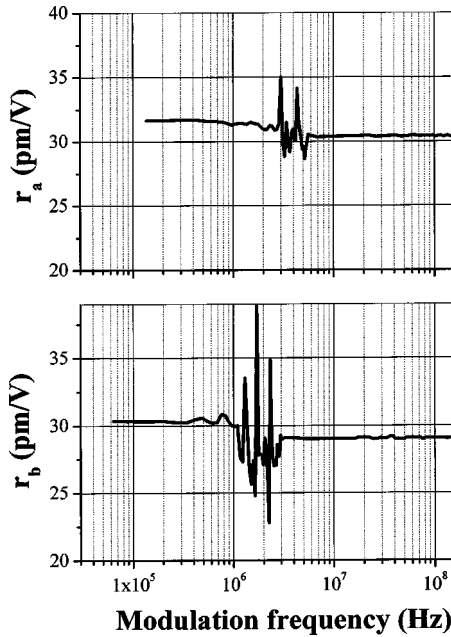


Fig. 5. Frequency dispersion of EO coefficients r_a and r_b deduced from time response measurements.

Table 1. Measured Values of the Unclamped (r^T) and Clamped (r^S) Effective EO Coefficients r_a , r_b , and r_c in 2A5NPLT at 632.8 nm

Coefficient	r^T (pm/V)	r^S (pm/V)	Acoustic Contributions ^a (%)
r_a	32 ± 1.5	30.5 ± 1.2	4.5
r_b	30.3 ± 1.2	29 ± 1.1	4.5
r_c	10 ± 0.5	—	—

^aThe last column lists the relative acoustic contribution to the EO coefficient and is defined by $(r^T - r^S)/r^T$.

Table 2. Comparison of the Low-Frequency EO Coefficients r_a , r_b , and r_c and of the Acoustic Contributions in 2A5NPLT and 2A5NPDP

Coefficient	2A5NPLT	2A5NPDP
r_a^T	32 ± 1.5	11 ± 1.2
r_b^T	30.3 ± 1.2	9.5 ± 1
r_c^T	10 ± 0.5	0.3 ± 0.04
$(r_a^T - r_a^S)/r_a^T$	4.5%	9%

All these values for r_a and r_b are reported in Table 1 as well as the low-frequency (10-kHz) value of coefficient r_c , which was measured with the ac modulation technique. As mentioned above it is obvious that the difference between the high- and the low-frequency values of both coefficients r_a and r_b is weak leading to a less than 5% acoustic contribution, which means that the EO effect in this compound originates essentially from electronic and ionic contributions.

The values of r_a and r_b are quite important since they are larger than those of lithium niobate, for example, $r_a = r_b = 20$ pm/V.²⁰ In contrast, the value of coefficient

r_c does not reach so large a value. This difference between r_a and r_b from one part and r_c from another part in the 2A5NPLT crystal is comparable with that observed for the 2A5NPDP crystal. Table 2 depicts this comparison. The anisotropy of the EO coefficient values in 2A5NPLT could be also attributed, as in 2A5NPDP, to anisotropy of the organic chromophore in its contribution to the polarizability.⁹

5. CONCLUSION

We have measured the frequency dispersion of EO coefficients r_a , r_b , and r_c of 2A5NPLT crystals. These results were compared with those of the 2A5NPDP crystal. We have observed a large increase of the values of the EO coefficients indicating a better alignment of the 2A5NP⁺ organic cations charge transfer axis in the 2A5NPLT crystal. The lattice deformation (giving rise to acoustic contribution in the EO properties) in 2A5NPLT is weak and even lower than those in 2A5NPDP. This could be explained by the denser 3-D hydrogen bond network in the 2A5NPLT crystal than in the 2A5NPDP crystal. We can guess, as we demonstrated in the case of 2A5NPDP crystal,⁹ that the magnitude of EO coefficients r_{13} , r_{23} , and r_{33} is mainly electronic in origin, arising from the π electron of the 2A5NP⁺ cations. Thus, contribution to the EO effect of the counter ions, tartrate anions for 2A5NPLT, and phosphates for 2A5NPDP is negligible for the EO properties.

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