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Origin of the Large Nonlinear Optical Susceptibility of 2-Amino-5-Nitropyridine-*L*-(+)-Tartrate

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The hyperpolarizabilities of 2-amino-5-nitropyridine-*L*-(+)-tartrate (ANPT) clusters that represent parts of the ANPT crystal have been calculated by a finite-field method using the semi-empirical AM1 Hamiltonian. Calculated results for several kinds of clusters have indicated that the hyperpolarizability in the crystal was strongly enhanced by two kinds of intermolecular interactions. One was the pyridinium-pyridinium interaction, and the other was the pyridinium-tartrate interaction. The former was dominantly contributed by the interaction among the pyridinium ions lying along their amino-to-nitro axis. The latter was the interaction between the hydrogen-bonded ions, and was suggested to include the intermolecular charge transfer. The enhanced hyperpolarizability was approximately three times as large as that without the interactions.

Keywords: Hyperpolarizability; finite-field method; AM1 calculation; intermolecular interaction, intermolecular charge transfer; molecular salt

1. INTRODUCTION

Nonlinear optical (NLO) materials have been intensively studied to develop optical devices, for example a frequency doubling device [1]. In particular, much attention has been paid to crystal materials with high second-harmonic generation (SHG) activity. Though several organic crystals with high SHG activity have been found so far, for example 2-methyl-4-nitroaniline (MNA) [2], their mechanical properties and processibility are insufficient as materials of the devices. The research for new organic crystals applicable to the devices is still in progress.

Molecular salts have been studied to search the applicable crystal [3–7], because salts are generally harder than molecular crystals. In these studies, it has been reported that 2-amino-5-nitropyridine-*L*-(+)-tartrate (ANPT) shows a large NLO coefficient, $d_{33} = 41$ pm/V, and a high degree of hardness, the Vickers hardness = 63 [7]. The aim of this study is to clarify an origin of the large d_{33} of the ANPT using molecular orbital calculations.

In the case of a conjugated molecule having both a donor group and an acceptor group, an intramolecular charge transfer leads to a large hyperpolarizability (β) [8–10]. Such molecules are called the charge-transfer molecules [8], and most organic crystals reported to show large NLO coefficients are composed of them.

2-Amino-5-nitropyridine, which is a raw material of the ANPT, is one of the charge-transfer molecules. However, an electronic structure of 2-amino-5-nitropyridinium ion in the ANPT is different from that of the 2-amino-5-nitropyridine, and the pyridinium ion is probably different from the charge-transfer molecules. *L*-(+)-Tartrate ion is also different from the charge-transfer molecules. Therefore the ANPT is expected to belong to a new type of a SHG crystal showing a large NLO coefficient. For this meaning, it is important to study the origin of the large d_{33} of the ANPT.

There have been some reports that an intermolecular interaction affects β [11–19]. For example, $|\beta_{zzz}|$ of a urea crystal has been calculated to be enhanced from 44 to 74 a.u. due to the intermolecular interaction [11]. In the case of solutions, β of some molecules are enhanced by more than one order of magnitude owing to the interactions [12]. β of the ANPT is also expected to be strongly enhanced by the interactions, because there are strong intermolecular interactions in the ANPT [6, 7]. Thus the intermolecular interactions should be considered in calculating the β of the ANPT.

The effects of the intermolecular interactions on β have been studied using three kinds of models: an external uniform electric field [12–14], a varying field using Coulombian point-charges located around a molecule [11], and a cluster of molecules [15–19]. Among the three of them, the last model can lead to the most precise results. In the model, several molecules are considered as a cluster in one calculation, and the interactions among these molecules can be taken into account. If the size of the cluster is large enough, calculated interactions can approximate those in the crystal.

To our knowledge, no cluster model with sufficiently large size was applied to a NLO crystal, because the calculation for a large cluster needs

huge computation power. Recently, progress in computer technology enabled the computation of a fairly large cluster. This paper presents calculated β of clusters, whose sizes are considered to be large enough to give information on the interactions in a crystal.

2. CRYSTAL STRUCTURE OF ANPT

The crystal structure of the ANPT has been determined by two groups independently [6, 7]. The structures reported by two groups agree in experimental errors, indicating validity of the estimations. In this paper, the geometrical parameters reported in ref. 7 were used in the calculations.

The ANPT crystal has a monoclinic unit cell ($a = 0.7611$ nm, $b = 0.9202$ nm, $c = 0.8241$ nm and $\beta = 96.48°$), and belongs to the space group $P2_1$. The unit cell consists of two 2-amino-5-nitropyridinium ions and two monohydrogentartrate ions. The pyridinium ions align approximately with their amino-to-nitro axis parallel to the two-fold screw axis, namely the b axis [6, 7].

The principal dielectric axes of the ANPT are related to the orientation of the pyridinium ions [7] as follows (see Fig. 2(b) in ref. 7); the Y and Z axes are approximately parallel to the pyridinium plane, and the Z axis is approximately parallel to the amino-to-nitro axis, where the principal refractive indices are obtained under the condition $n_z > n_y > n_x$. This relation represents that the π electrons of the pyridinium ions contribute dominantly to the polarizability, like neutral charge-transfer molecules, such as MNA. Accordingly, it is supposed that these π electrons also contribute dominantly to β, and that the maximum component of the β tensor is β_{zzz}.

In the ANPT crystal, ions are strongly connected by intermolecular hydrogen-bonds (see Fig. 1 (a) in ref. 6 and Fig. 2 (b) in ref. 7). Each tartrate ion has both a carboxylate group and a carboxyl group. The former group is hydrogen-bonded to a carboxyl group in a neighbouring tartrate ion, while the latter group is hydrogen-bonded to a carboxylate group in another neighboring tartrate ion. These hydrogen-bonds build helical chains of tartrate ions. Moreover, there are also two kinds of hydrogen-bonds connecting each pyridinium ion with a neighboring tartrate ion. One is between a hydrogen atom attached to a nitrogen atom in a pyridine ring and a carboxyl group in the tartrate ion. The other is between an amino group in the pyridinium ion and a hydroxyl group in the tartrate ion. These intermolecular hydrogen-bonds are presumed to have effects on β.

3. METHODS

3.1. Computational Details

Spin-restricted calculations were performed by the MOPAC 6.0 program [20–21] using the semi-empirical AM1 Hamiltonian, whose parameters are optimized to reproduce experimental values of molecular properties, for example heats of formation and dipole moments [22]. The experimental values used in the parametrization can be accurately reproduced by *ab initio* calculations when electron correlation is considered. Therefore, to the extent of the approximation used in the AM1 method, the AM1 calculations are considered to give the results including electron correlation even if the calculations do not include electron correlation explicitly.

Static β were calculated by a finite-field method implemented in the MOPAC program [23]. Atomic charges in the presence of an external electric field were also calculated. The strength of the external electric field was the same as that used in the calculation of β.

ANPT clusters, namely the calculated models of the ANPT crystal, were composed of hydrogen-bonded pyridinium-tartrate ion pairs. Geometries of the ANPT clusters were extracted from the ANPT crystal structure determined by X-ray structure analysis [7]. β of several kinds of clusters were compared with each other, and effects of intermolecular interactions were examined.

Moreover, β of pyridinium clusters, which corresponded to pyridinium-ion parts of the ANPT crystal, were calculated to estimate the contribution of the pyridinium ions. Tartrate clusters, which corresponded to tartrate-ion parts of the ANPT crystal, were also calculated. Total charges of the pyridinium clusters were equated with the numbers of the pyridinium ions, because total charge of each pyridinium ion was 1 in the calculation of the ANPT cluster. For similar reason, total charges of the tartrate clusters were set to be negative, and absolute values of them were equated with the numbers of the tartrate ions.

Though calculations of anions are generally more difficult than those of netural molecules, the AM1 method has been reported to be applicable to anions as well as netural molecules and cations [22]. In the AM1 calculations of anions, serious problems arise only when the charge on an atom approaches -1 [22]. In the case of the present study, the smallest atomic charge was -0.62, which was the charge on oxygen of a carboxylate group. Accordingly, the AM1 method is considered to be applicable to calculations of the ANPT, which includes both anions and cations.

In the calculation of β using the finite-field method, total energy of the system is calculated in the presence of an external electric field. The total energy includes the interaction between the field and the dipolemoment of the system. A dipolemoment of a charged cluster depends on a choice of origin of the coordinate system. On the other hand, the calculated β is independent of the choice, because the β is related to the change of the dipolemoment induced by the field.

In order to confirm reliability of the calculation of β, d_{33} was estimated from calculated β_{zzz}, and compared with the observed value. d_{33} is given by [24]

$$d_{33} = \frac{1}{2V} \times \left(\frac{n_\omega^2 + 2}{3} \right)^2 \times \frac{n_{2\omega}^2 + 2}{3} \times \beta_{UC} \tag{1}$$

where V is the volume of the unit cell, n_ω is the refractive index at a fundamental wavelength, $n_{2\omega}$ is the refractive index at a second-harmonic wavelength, and β_{UC} is β_{zzz} of the unit cell.

3.2. Models of ANPT

Four kinds of ANPT clusters, which are shown in Figure 1 and denoted as A, B, C and D, were used for the calculations. The model A_1 consists of a pyridinium-tartrate ion pair that are hydrogen-bonded with each other. Other models correspond to expansion of A_1. The models A_2, A_3 and A_4 correspond to alignments of two, three and four sets of A_1, respectively (A_2 is shown in Fig. 1). The expanding direction of these models is the [010] direction, which is nearly parallel to the amino-to-nitro axis.

The model $X_i (X = B, C, D; i = 1 - 3)$ corresponds to expansion of A_i. The expanding direction for B_i is the [100] direction, while that for C_i and D_i is parallel to the Y axis, which is perpendicular to the b axis and parallel to the plane of pyridine ring. The essential difference between C_i and D_i is a position of the tartrate ions. The tartrate ions in C_i are hydrogen-bonded with each other, whereas those in D_i are not.

The structures of these models can be easily understand by noting positions of the pyridinium ions. The pyridinium ions in $A_i (i = 1 - 4)$ align along the [010] direction with their pyridine rings lying in a plane. The pyridinium ions in $B_i (i = 1 - 3)$ make two stacked alignments, which are superposed in the view along the [100] direction, as shown in Figure 1

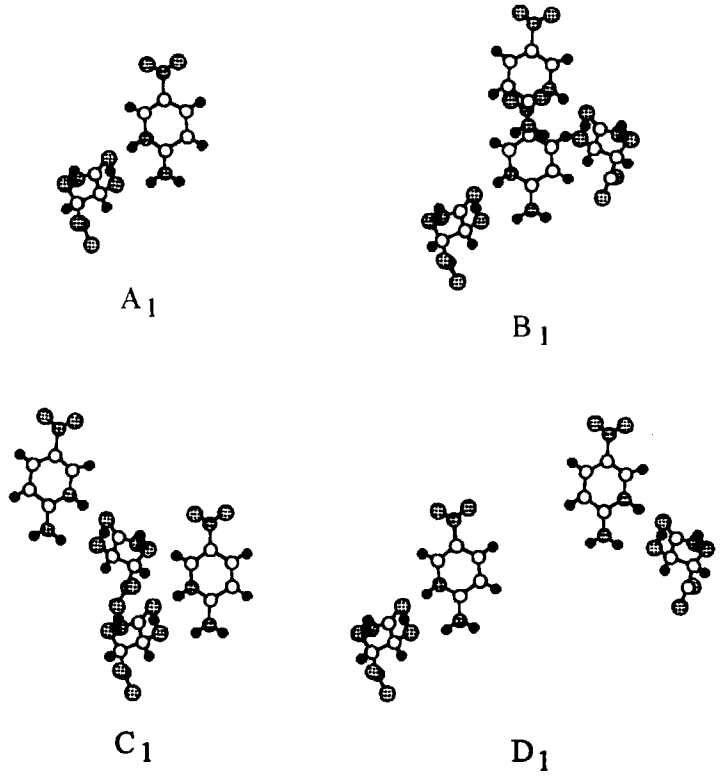

FIGURE 1a Calculated cluster models viewed along the [100] direction.

for B_2. On the other hand, the pyridinium ions in C_i and D_i ($i = 1 - 3$) make two parallel alignments with all of their pyridine rings lying in a plane.

When the calculated β of several models are compared with each other, the effects of the intermolecular interactions on β can be examined. In the case of the models A_1, A_2, A_3 and A_4, the interactions among the molecules lying along the [010] direction can be examined. Likewise, the comparison among X_1, X_2 and X_3 ($X = B, C, D$) can give such information. On the other hand, the comparison between A_i and $X_i (X = B, C, D)$ can give information for the interactions among the molecules lying along its expanding direction, namely the [100] direction for B_i, and the direction parallel to the Y axis for C_i and D_i. Moreover, the comparison between C_i and D_i can also give information for the intermolecular hydrogen-bond between the tartrate ions.

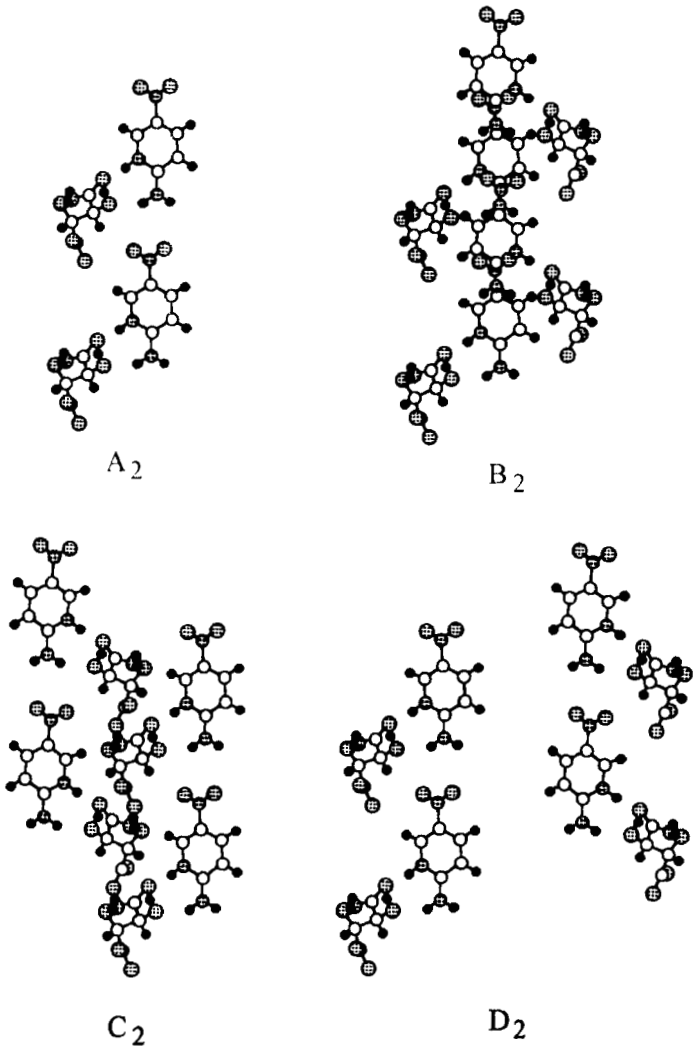

FIGURE 1b Calculated cluster models viewed along the [100] direction.

4. RESULTS AND DISCUSSION

4.1. Hyperpolarizabilities of Isolated Molecules

First, β_{zzz} without intermolecular interactions were calculated for the 2-amino-5-nitropyridinium ion and the L-(+)-tartrate ion. For comparison, those of 2-methyl-4-nitroaniline (MNA) and 2-amino-5-nitropyridine

(2A5NPy) were also calculated. Results are listed in Table I. Geometries of calculated ions were the same as those in the ANPT crystal, while geometries of MNA and 2A5NPy, were optimized in the molecular orbital calculations. In the case of MNA and 2A5NPy, Z axis was taken to be parallel to the amino-to-nitro axis, similarly to the pyridinium ion.

The β_{zzz} of 2A5NPy was approximately equal to that of MNA, as was expected from their structural similarity. On the other hand, the β_{zzz} of the pyridinium ion was much smaller than that of 2A5NPy. This result suggests that there is no effective charge-transfer between amino and nitro groups in the pyridinium ion. The β_{zzz} of the tartrate ion was nearly a half of the pyridinium ion.

4.2. Hyperpolarizabilities of ANPT Clusters

The calculated β_{zzz} of clusters are summarized in Table II, where β_{ANPT} denotes β_{zzz} per the unit cell, and β_{Py} and β_{Ta} denote the contribution of the pyridinium ions and the tartrate ions in the β_{ANPT}, respectively. The β_{Py} and the β_{Ta} were estimated by the calculations for the pyridinium clusters and the tartrate clusters, respectively. The β_{zzz} was the maximum component in the β tensor, as was supposed in chapter 2. Other components of the β tensor were smaller than 11% of β_{zzz}.

β_{ANPT} of A_1, A_2, A_3 and A_4 were increasing in this order with model's expansion. Such increase could be also found for other series of models; for example, β_{ANPT} of B_2 was larger than that of B_1, and that of B_3 was still larger. These results represent that β_{ANPT} is strongly enhanced by the interactions among the ions lying along the [010] direction. Due to these interactions, β_{ANPT} of A_4 was enhanced from 6.1×10^{-30} esu, which was the value of A_1, to 9.2×10^{-30} esu. The difference in β_{ANPT} between A_3 and A_4 was small, and was smaller than the difference between A_2 and A_3. Therefore, the increase of the A_i series seems to be nearly saturated in A_4.

TABLE I Calculated hyperpolarizabilities β_{zzz} of isolated molecules

molecule	$\beta_{zzz}[10^{-30}\text{esu}]$
2-methyl-4-nitroaniline[a]	5.2
2-amino-5-nitropyridine[a]	5.4
2-amino-5-nitropyridinium ion	1.1
L-(+)-tartrate ion	0.5

[a]Geometry is optimized in a molecular orbital calculation.

TABLE II Calculated hyperpolarizabilities β of various models in 10^{-30} esu. β_{ANPT} denotes β_{zzz} per unit cell. β_{Py} and β_{Ta} correspond to contributions of the pyridinum and tartrate molecules in β_{ANPT}, respectively

model	β_{ANPT}	β_{Py}	β_{Ta}
A_1	6.1	2.1	0.9
A_2	7.9	3.8	1.1
A_3	8.7	4.7	1.2
A_4	9.2	5.2	1.2
B_1	6.3	2.3	1.1
B_2	8.8	4.4	1.2
B_3	10.1	5.8	1.2
C_1	5.7	1.9	0.8
C_2	7.7	3.5	0.7
C_3	8.4	4.4	0.7
D_1	6.0	2.0	1.1
D_2	7.8	3.7	1.2
D_3	8.6	4.6	1.2

β_{ANPT} of B_1, B_2 and B_3 were larger than those of A_1, A_2 and A_3, respectively. This result shows that β_{ANPT} is also enhanced by the interactions among the ions lying along the [100] direction. β_{ANPT} of A_i ($i = 1, 2, 3$) was approximately equal to those of C_i and D_i. This suggests that the interactions among the ions lying along the Y axis have very small effects on β_{ANPT}.

The maximum value of β_{ANPT} was 10.1×10^{-30} esu of B_3. This value is considered to be a best approximation of β_{ANPT} in this study, because B_3 represents both large effects of the intermolecular interactions. The real value is expected to be somewhat larger than that value.

The relationship among β_{Py} of various models was similar to the case of β_{ANPT}. The interactions among the ions lying along the [010] direction indicated a dominant effect on β_{Py}. These interactions enhanced β_{Py} from 2.1×10^{-30} esu (A_1) to 5.2×10^{-30} esu (A_4). This enhancement agrees with the calculated results of linear *p*-nitroaniline dimers [16], though the pyridinium ion is not the charge-transfer molecule. β_{Py} was also enhanced by the interactions among the pyridinium ions lying along the [100] direction. Because of these interactions, β_{Py} of B_3 was larger than that of A_3 by 0.9×10^{-30} esu. On the other hand, β_{Py} of C_i and D_i ($i = 1, 2, 3$) were nearly equal to that of A_i.

Since β_{Py} of A_1 was estimated for an isolated pyridinium ion, the value (2.1×10^{-30} esu) represents the contribution of the pyridinium ion without the intermolecular interaction. β_{Py} of B_3 is considered to be a best approximation of β_{Py} in this study, becuase B_3 represents both large effects of the

pyridinium-pyridinium interactions. β_{Py} of B_3 was larger than that of A_1 by ca. 4×10^{-30} esu, which is considered to be the contribution of the pyridinium-pyridinium interactions in the β_{ANPT}.

β_{Ta} of A_1 (0.9×10^{-30} esu) represents the contribution of the tartrate ion without the intermolecular interaction, because it was estimated for an isolated tartrate ion. β_{Ta} was reduced by the interaction between hydrogen-bonded tartrate ions, while β_{ANPT} and β_{Py} were strongly enhanced by the intermolecular interactions, as described above. Due to that interaction, β_{Ta} of C_3 was smaller than that of A_1 by 0.2×10^{-30} esu. Since the difference in β_{Ta} between A_1 and any model was very small, the contribution of the tartrate-tartrate interactions is considered to be negligibly small.

β_{Py} of A_1 was ca. twice as large as β_{Ta} of A_1. In this case, the intermolecular interactions have no effect on both β_{Py} and β_{Ta}. The intermolecular interactions increased the difference between β_{Py} and β_{Ta}. In the case of C_3, β_{Py} was ca. six times as large as β_{Ta}.

The addition of β_{Py} and β_{Ta} for A_1 (3.0×10^{-30} esu) represents β_{ANPT} without the intermolecular interaction. The addition of β_{Py} and β_{Ta} was smaller than β_{ANPT} by ca. 3×10^{-30} esu for each model. This value is due to the contribution of the pyridinium-tartrate interactions. Considering that each model consists of the hydrogen-bonded pyridinium-tartrate ion pairs, the pyridinium-tartrate interactions contributing to β_{ANPT} are the interactions between hydrogen-bonded ions.

It was summarized that β_{ANPT} was found to be approximated by the sum of three contributions as follows:

$$\beta_{ANPT} \fallingdotseq \beta_{ANPT}{}^{0} + \beta_{Py-Py} + \beta_{Py-Ta}$$

where $\beta_{ANPT}{}^{0}$ is β_{ANPT} without the intermolecular interactions, β_{Py-Py} is the contribution of the pyridinium-pyridinium interactions, and β_{Py-Ta} is that of the pyridinium-tartrate interactions. $\beta_{ANPT}{}^{0}$, β_{Py-Py} and β_{Py-Ta} were estimated to be 3, 4 and 3×10^{-30} esu, respectively.

4.3. Atomic Charges In the Presence of Electric Field

The discussion in above sections shows that β_{ANPT} is mainly influenced by two kinds of interactions, namely the pyridinium-pyridinium interaction and the pyridinium-tartrate interaction. To investigate the interactions more precisely, atomic charges with an external electric field along the nitro-to-amino direction were calculated.

In the case of the pyridinium clusters, the total charge of each ion with the field was estimated to be 1, which was the same as that without the field. This result shows that there is no intermolecular charge transfer between the pyridinium ions induced by the field. On the other hand, in the case of the ANPT clusters, the total charge of each pyridinium ion with the field was decreased from that without the field, and the total charge of each tartrate ion was increased. These changes in the total charges of ions can be seen in Figure 2, which shows the calculated charge deviations of A_1 induced by the field. Totals of the charge deviations in the pyridinium ion and the tartrate ion were negative and positive, respectively. These results imply that there is charge transfer between the pyridinium and tartrate ions.

Subsequently, an addition of the charge deviation induced by the field along the amino-to-nitro direction and the deviation induced by the opposite field was calculated for each atom. The additions are considered to represent the nonlinear response against the field. For example, in the case of MNA, electrons can move from the amino group to the nitro group more easily than in the opposite direction. This anisotropy causes the total of the additions in the nitro group to be negative, and the total in the amino group to be positive.

Figure 3 shows the calculated additions for A_1. Total of the additions in the pyridinium ion was negative, and that in the tartrate ion was positive. This result suggests that the charge transfer from the pyridinium ion to the

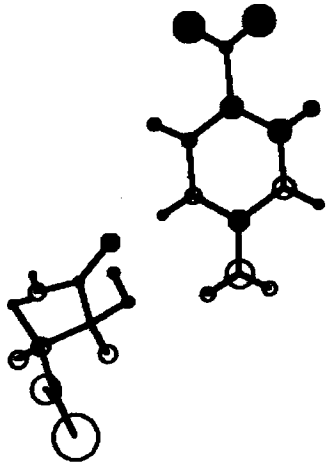

FIGURE 2 Charge deviations of the model A_1 induced by an electric field along the nitro-to-amino direction. Open and filled circles correspond to positive and negative quantity of the deviations, respectively.

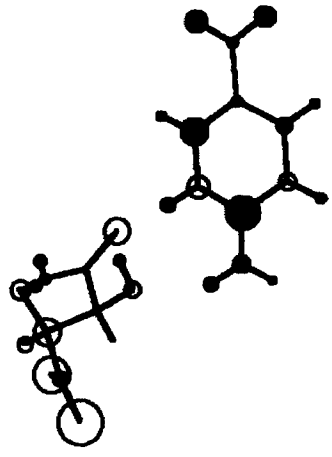

FIGURE 3 Addition of the charge deviations induced by an electric field along the amino-to-nitro direction and that induced by opposite field for the model A_1. Open and filled circles correspond to positive and negative quantity of the additions, respectively.

tartrate ion can happen more easily than that in the opposite direction, and that the charge transfer contributes to β_{ANPT}.

4.4. Calculation of d_{33}

d_{33} of the ANPT was calculated using equation (1) from calculated β_{UC}, observed unit-cell volume ($573.5 \times 10^{-30}\,m^3$) and refractive indices (1.730 at 1064 nm, 1.835 at 532 nm) [7]. β_{ANPT} of B_3 was used as β_{UC}. The resultant d_{33} was obtained as 18 pm/V. This value is ca. a half of the observed d_{33} (41 pm/V) [7]. The discrepancy between calculated and observed d_{33} is considered to be arisen dominantly from the following reasons; the calculated β_{UC} corresponds to β_{UC} at an infinite wavelength, while the fundamental wavelength of the observation is 1064 nm. β_{UC} at 1064 nm is expected to be larger than the β_{UC} at the infinite wavelength. β of *p*-nitroaniline at 1060 nm has been reported to be ca. 1.8 times as large as β at 1907 nm [25], which seems to be nearly equal to β at an infinite wavelength. If dispersion of β of ANPT is similar to that of *p*-nitroaniline, the β_{ANPT} calculated in this study agrees well with the observed d_{33}.

5. CONCLUSION

In the ANPT crystal, the alignments of the pyridinium ions are sandwiched between the layers of the tartrate ions [6, 7]. Though β of the tartrate ions

are much smaller than those of the pyridinium ions, the tartrate ions seem to play an important role to form the crystal structure. Moreover, the tartrate ions were revealed in this study to contribute to β through the pyridinium-tartrate interactions, which were suggested to include the intermolecular charge-transfer. The calculated strong enhancement of β indicates that the crystal structure of ANPT is efficient in enhancing β, and that such enhancement is the origin of the large nonlinear-optical susceptibility.

Molecular salts have large probability to cause strong enhancement of β, because intermolecular interactions are strong in them. The contribution of the intermolecular charge-transfer to β seems to be characteristic of molecular salts. In the case of 2-amino-5-nitropyridine, the calculation shows that the ionization reduces β. Molecular salts composed of molecules whose β are enlarged by ionization are expected to represent larger SHG coefficients than ANPT.

References

[1] *Nonlinear Optical Properties of Organic Molecules and Crystals Vol. 1 and 2*, Ed. D. S. Chemla and J. Zyss (Academic Press, New York, 1987).
[2] B. F. Levine, C. G. Bethea, C. D. Thurmond, R. T. Lynch and J. L. Bernstein, *J. Appl. Phys.*, **50**, 2523 (1979).
[3] G. R. Meredith, *ACS Symp. Ser.*, **233**, p. 27 (1983).
[4] S. R. Marder, J. W. Perry and W. P. Schafer, *Science*, **245**, 627 (1989).
[5] R. Masse and J. Zyss, *Mol. Eng.*, **1**, 141 (1991).
[6] J. Zyss, R. Masse, M. Bagieu-Beucher and J. P. Levy, *Adv. Mater.*, **5**, 120 (1993).
[7] O. Watanabe, T. Noritake, Y. Hirose, A. Okada and T. Kurauchi, *J. Mater. Chem.*, **3**, 1053 (1993), *ibid.*, **4**, 993 (1994).
[8] J. Zyss and D. S. Chemla, in Ref. 1, p. 23.
[9] B. F. Levine, *Chem. Phys. Lett.*, **37**, 516 (1976).
[10] J. L. Oudar and D. S. Chemla, *J. Chem. Phys.*, **66**, 2664 (1977).
[11] J. Zyss and G. Berthier, *J. Chem. Phys.*, **77**, 3635 (1982).
[12] I. A. Maslianitsin, V. D. Shigorin and G. P. Shipulo, *Chem. Phys. Lett.*, **194**, 355 (1992).
[13] C. C. Teng and A. F. Garito, *Phys. Rev. Lett.*, **50**, 350 (1983).
[14] C. C. Teng and A. F. Garito, *Phys. Rev. B.*, **28**, 6766 (1983).
[15] C. W. Dirk, R. J. Twieg and G. Wagnière, *J. Am. Chem. Soc.*, **108**, 5387 (1986).
[16] T. Yasukawa, T. Kimura and M. Uda, *Chem. Phys. Lett.*, **169**, 259 (1990).
[17] S. D. Bella, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, **114**, 5842 (1992).
[18] S. D. Bella, I. L. Fragal, M. A. Ratner and T. J. Marks, *J. Am. Chem. Soc.*, **115**, 682 (1993).
[19] J. Waite and M. G. Papadopoulos, *Z. Naturforsch*, **45a**, 189 (1990).
[20] J. J. P. Stewart, MOPAC 6.0, QCPE#455 (1990).
[21] J. J. P. Stewart, *J. Computer-Aided Mol. Design*, **4**, 1 (1990).
[22] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).
[23] H. A. Kurtz, J. J. P. Stewart and K. M. Dieter, *J. Comp. Chem.*, **11**, 82 (1990).
[24] D. S. Chemla, J. L. Oudar and J. Jerphagnon, *Phys. Rev. B*, **12**, 4534 (1975).
[25] C. C. Teng and A. F. Garito, *Phys. Rev. B*, **28**, 6766 (1983).