Theoretical Evaluation of Hyperpolarizability of L-2-Pyrrolidone-5-carboxylic Acid (L-PCA)

Manabu Kitazawa,* Mitsuo Takahashi, Tatsuo Wada,† Hiroyuki Sasabe,† Masayoshi Nakano,†† and Kizashi Yamaguchi††

Central Research Laboratories, Ajinomoto Co., Inc., Suzuki-cho 1-1, Kawasaki-ku, Kawasaki, Kanagawa 210

†Frontier Research Program, The Institute of Physical and Chemical Research (RIKEN), Hirosawa 2-1, Wako, Saitama 351-01

††Department of Chemistry, Faculty of Science, Osaka University, Machikaneyama-cho 1-1, Toyonaka, Osaka 560

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L-2-Pyrrolidone-5-carboxylic acid (L-PCA) is a novel nonlinear optical material with the optical transparent range down to the UV region. L-PCA molecules are hydrogen-bonded to form the three-dimensional network in a crystal. It has been thought that the network of hydrogen bonds influences on the stability of the crystal structure as well as the second-order optical nonlinearity. We have performed the theoretical evaluation of the contributions of the intermolecular hydrogen bonds to structural stability and second-order nonlinearity in the L-PCA crystals by use of the molecular orbital calculation methods. In the calculation of CNDO/S-SECI (singly excited configuration interaction) method, it is shown that the primary contributor to the molecular hyperpolarizability (β) is an $n_\pi \rightarrow \pi^*$ transition in the amide moiety of L-PCA molecule. The calculation of intermolecular interaction energies for L-PCA clusters by the ab initio STO-3G method indicates that the hydrogen bonds in the crystal contribute to the stabilization of the crystal structure by -7.8 to -9.1 kcal mol^{-1} for one hydrogen-bond formation. Furthermore, it is also confirmed by CNDO/S-CHF (coupled Hartree–Fock) calculation that the hydrogen-bonding interactions induce the enhancement of the β_{XYZ} value, a unique β component contributing to the nonlinear optical coefficient (d_{14}). On the basis of the calculated β components, d_{14} can be estimated to be d_{14}=0.30 pm V^{-1} by the oriented-gas model. This value is in good agreement with the experimental result. Therefore, these results verify that the hydrogen bonds between L-PCA molecules contribute not only to the physical and chemical stability of L-PCA crystals but also to the enhancement of β values. This theoretical estimation shows the effectiveness of the hydrogen bonds in second-order nonlinear optical crystals.

In recent years, since the large nonlinear optical effects were found in many organic crystals, these materials have been studied intensively for applications such as second-harmonic generation (SHG), electrooptic modulation, sum- and difference-frequency generation and optical parametric oscillation.[1] In particular, those organic materials are expected to be useful for frequency up-conversion of conventional lasers. High nonlinearities are found in the molecules with extended conjugated π-electron systems and donor-acceptor groups at para positions such as nitroanilines.[2] Although these type molecules possess large second-order molecular hyperpolarizabilities (β), they exhibit no second-order optical nonlinearities in crystals because of centrosymmetric packing. In general, molecules which possess a large β value have the tendency to crystallize in centrosymmetric packing structures due to the cancellation of their large permanent dipole moments, and thus exhibit the vanishing SHG coefficient in the crystals.[3] Various molecular design approaches have been applied to prevent centrosymmetric packing in the crystal. For example, the combination of a moderately long π-electron conjugated system and a relatively weak electron donor such as the methoxy, bromo or iodo group is one of the effective approaches to the design of efficient SHG crystals.[4—6] Following this guiding principle, we investigated the powder SHG efficiencies[7] of many organic materials having a moderately long π-electron conjugate system without a strong polar group. Some azlactone derivatives (2,4-substituted 5-oxazolinone) have been found to show high powder SHG efficiencies and it has been clarified that the backbone skeleton of the derivatives have an advantage in noncentrosymmetric packing in the crystals.[8] However, the azlactone derivatives as well as the other organic materials based on the guiding principle possess the cutoff wavelength beyond 400 nm. The narrow optical transparency may limit the application of these organic crystals to frequency up-conver-

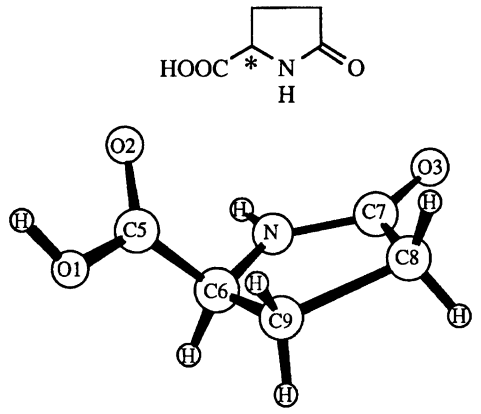

Fig. 1. Molecular structure of L-PCA.

sion. The narrow optical transparency comes from the fact that in those molecules the β value finds its origin in a $\pi \rightarrow \pi^*$ transition and the transition energy value (3.5—4.0 eV) corresponds to the absorption maxima wavelength at about 350 nm.

Urea has been known as a nonlinear optical crystal which has relatively large nonlinear optical coefficients ($d_{14}=1.7$ pm V^{-1}) and a short cutoff wavelength (200 nm).[9] The primary contributor to the β value is estimated to be an $n_\pi \rightarrow \pi^*$ transition in the amide moiety of urea molecule.[10] However urea crystals are very difficult to grow to a large size, chemically unstable due to the hygroscopic property and mechanically soft. It is expected that hydrogen bonds have an effect on physical properties of a crystal such as mechanical hardness, melting point and chemical stability. From the structural point of view we investigated the powder SHG efficiencies[7] of many organic materials which possess an $n_\pi \rightarrow \pi^*$ transition as primary contributor to the β value and hydrogen bonds between molecules, such as amino acids, peptides, nucleic acids and their derivatives. In our previous work[11] L-2-pyrrolidone-5-carboxylic acid, that is abbreviated hereafter as L-PCA (The designation in the IUPAC nomenclature is (*S*)-2-oxopyrrolidine-5-carboxylic acid), has been found to show the same degree of SHG efficiency as urea in the powder form. L-PCA is one of the cyclic amino acids and the structural formula is shown in Fig. 1. L-PCA crystal is transparent up to 260 nm. This transparency over wide range makes it possible to generate nonlinear frequency into the ultraviolet region. The phase-matching condition for SHG and SFM process can be achieved well into the UV region (the shortest wavelength of up to 266 nm) where only a few nonlinear optical crystals are available.[12] By X-ray diffraction analysis L-PCA crystals have been found to be in the orthorhombic system with space group symmetry $P2_12_12_1$ with the unit cell lattice parameters: $a=9.010(0)$, $b=13.422(0)$, $c=14.640(8)$ Å, and to contain three L-PCA molecules in the asymmetric unit. The observed data including the atomic coordinates are identical to those reported by van Zoeren et al.[13] Here in our notation the principal dielectric axes *X*, *Y*, and *Z* are parallel to the crystallographic axes *b*, *a*, and *c*, respectively. We reported also that it is easy to grow L-PCA single crystals to a large size and crystals are chemically stable at ambient condition because molecules are hydrogen-bonded to form the three-dimensional network in a crystal. In addition, this network of hydrogen bonds stabilizes the crystal structure; the melting point was measured to be 162—163 °C, which is very high compared with other

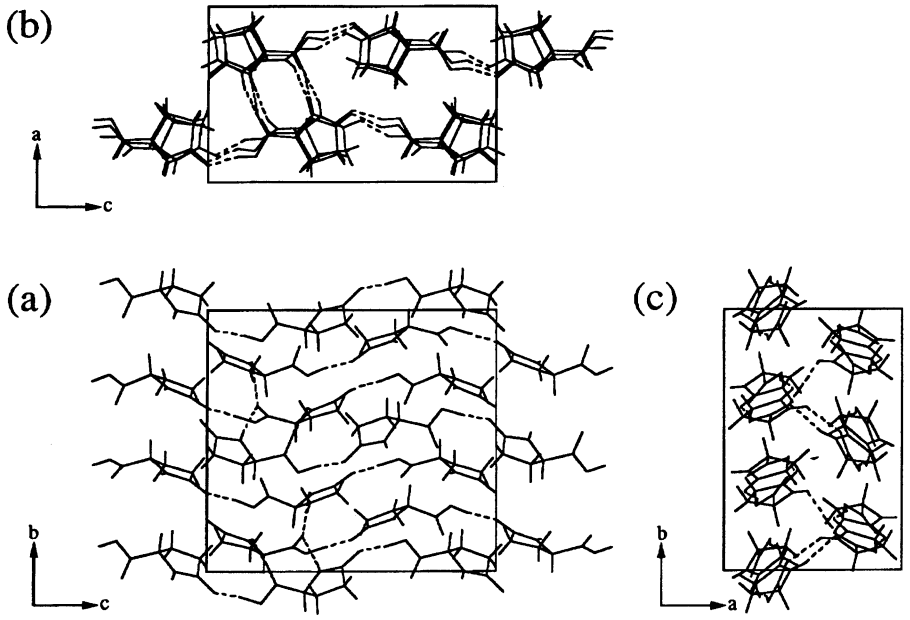

Fig. 2. Crystal structure of L-PCA viewed down along (a) the *a* axis, (b) the *b* axis, and (c) the *c* axis. The hydrogen bonds are represented by broken lines and form the three dimensional network (These crystal structure data are taken from the Cambridge Structural Database System (Ref. 28)).

organic nonlinear optical crystals and the mechanical hardness was measured to be about 33 by the Vickers method whose value is much larger than that of urea (about 9). However, the details of the contributions of the hydrogen bond to the crystal structure and the β values have not been elucidated yet.

This paper presents the theoretical evaluation of the contributions of intermolecular hydrogen-bond interactions to chemical stability and second-order optical nonlinearity in L-PCA crystals. Firstly, it is shown that the primary contributor to the β value is an $n_\pi \rightarrow \pi^*$ transition by the use of CNDO/S-SECI calculation method.[14] Secondly, the intermolecular interaction energies (ΔE) in L-PCA crystals are calculated by the ab initio method at STO-3G level and the structural stabilization by the hydrogen bonds are estimated quantitatively. Thirdly, we performed the CNDO/S-CHF calculation[15] in order to investigate the contributions of the hydrogen bond to the β values. It is estimated that the β_{XYZ} value is enhanced about 55% by the hydrogen bonds in L-PCA crystals. The β_{XYZ} value only contributes to d_{14} value, a unique nonvanishing nonlinear coefficient. Finally, the β_{XYZ} values are also used to estimate the d_{14} value based on the oriented gas model description.[16] This theoretically predicted value of d_{14} agreed well with that obtained by the experimental measurements.

Method of Calculation

The β Values of L-PCA Molecule. Theoretical calculations of the β values were performed by the all-valence-electron semiempirical CNDO/S-SECI method. It has already been proven that the β values calculated by this method agree very well with the measured values of p-nitroaniline, urea, etc.[17—19] The formulation of the CNDO/S-SECI method can also be used to elucidate the relationship between a molecular structure and the origin and mechanism of hyperpolarizability in term of the molecular orbital description. This method involves an initial configuration interaction treatment of ground- (g) and excited-state (n and n') wave functions. The expression for the individual components of β can be written in terms of transition moments and excitation energies as

$$\beta_{ijk}+\beta_{ikj}=-\frac{e^3}{4\hbar^2}\sum_{n\neq n'}\left\{\left(r^j_{gn'}r^i_{n'n}r^k_{gn}+r^k_{gn'}r^i_{n'n}r^j_{gn}\right)\left[\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}+\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}-\omega)}\right]+\left(r^i_{gn'}r^j_{n'n}r^k_{gn}+r^i_{gn'}r^k_{n'n}r^j_{gn}\right)\left[\frac{1}{(\omega_{n'g}+2\omega)(\omega_{ng}+\omega)}+\frac{1}{(\omega_{n'g}-2\omega)(\omega_{ng}-\omega)}\right]\right.$$

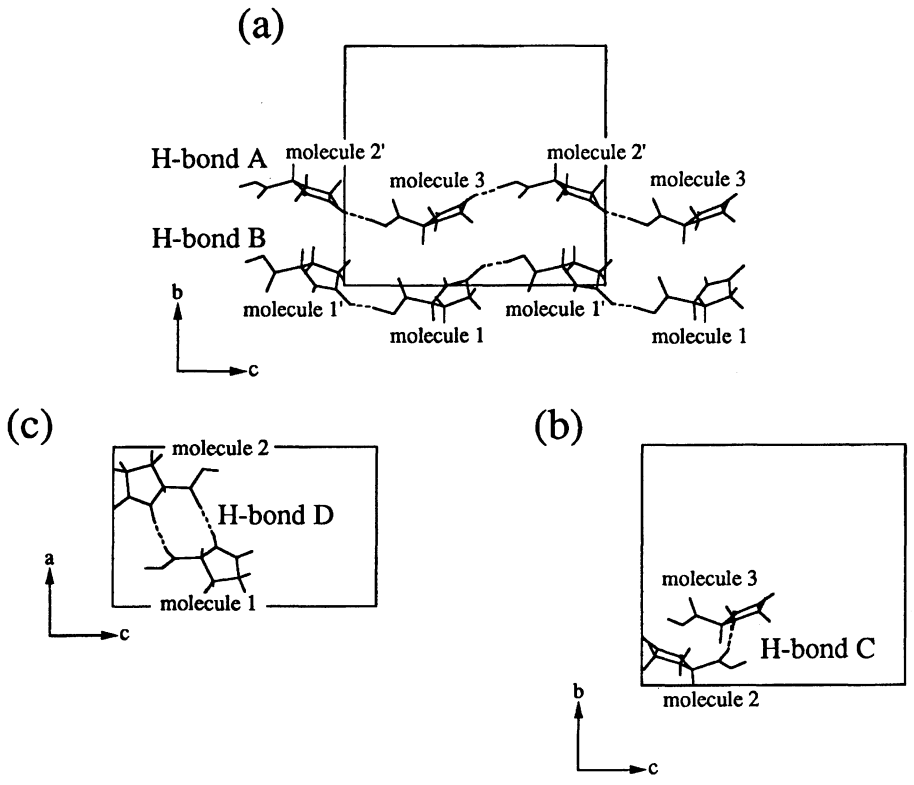

Fig. 3. Four types of hydrogen bonds [O(3)]···[H(O1)] and [H(N)]···[O(2)]. (a) H-bond A and B, (b) H-bond C, and (c) H-bond D. The hydrogen bonds are represented by broken lines (These crystal structure data are taken from the Cambridge Structural Database System (Ref. 28)).

$$+\left(r^j_{gn'}r^k_{n'n}r^i_{gn}+r^k_{gn'}r^j_{n'n}r^i_{gn}\right)\left[\frac{1}{(\omega_{n'g}-\omega)(\omega_{ng}-2\omega)}+\frac{1}{(\omega_{n'g}+\omega)(\omega_{ng}+2\omega)}\right]+4\sum_n\left[r^j_{gn}r^k_{gn}\Delta r^i_n\left(\omega^2_{ng}-4\omega^2\right)+r^i_{gn}\left(r^k_{gn}\Delta r^j_n+r^j_{gn}\Delta r^k_n\right)\left(\omega^2_{ng}+2\omega^2\right)\right]\frac{1}{(\omega^2_{ng}-\omega^2)(\omega^2_{ng}-4\omega^2)}\Bigg\}, \quad (1)$$

where e is the charge of electron, ω is the frequency of the applied radiation field, $r^i_{n'n}$ $(=<n'|r^i|n>)$ is the matrix element of the displacement operator r^i along the ith molecular axis between the excited-state wave functions ($|n'>$ and $|n>$), Δr^i_n $(=r^i_{nn}-r^i_{gg})$ is related to the difference between the excited- and ground-state dipole moments ($\Delta\mu^i_n=-e\cdot\Delta r^i_n$), and $\hbar\omega_{ng}$ is the magnitude of the transition energy between the excited- and ground-states.[19] Now, the vector components ($\beta_i:i=x,y,z$) of β are expressed by the following formula[20]

$$\beta_i=\beta_{iii}+\frac{1}{3}\sum_{j\neq i}(\beta_{ijj}+\beta_{jji}),\ i,j=x,y,z \quad (2)$$

and the magnitude of β is given by

$$|\beta|=\left(\beta^2_x+\beta^2_y+\beta^2_z\right)^{1/2}. \quad (3)$$

β_M, the projection of the vector β onto the permanent dipole moment corresponds to the measured β value obtained by the EFISH method. Geometrical parameters of L-PCA were taken from the crystallographic data as described in Ref. 13.

The ΔE Values of L-PCA Clusters. Quantitatively accurate estimations of weak intermolecular interaction energies between large molecules are still difficult because applicable computational methods are very limited. Recently, Tsunekawa and Yamaguchi reported that the ab initio calculations at STO-3G level were successful for estimating intermolecular interaction energies in the 3,9-dinitro-5a,6,11a,12-tetrahydro[1,4]benzoxazino[3,2-*b*][1,4]benzoxazine (DNBB) clusters forming hydrogen-bonded chains between the amino and the nitro groups.[21] Moreover it was shown in the same paper that the hydrogen bonds play crucial roles for the crystal structure and molecular packing in DNBB crystals. The molecular packing of L-PCA crystals seems to be tailored by the intermolecular hydrogen bonds between the amide oxygen [O(3)] and the carboxyl hydrogen [H(O1)] (1.73 Å), forming a head-to-tail hydrogen-bonded chain, parallel to the *c* axis and lying in the *bc* plane as shown in Fig. 2(a). Moreover another hydrogen bond exists between the amide hydrogen [H(N)] and the carbonyl oxygen [O(2)] (2.30 Å) giving rise to interaction between the above mentioned chains. Here STO-3G calculations were also done for evaluation of intermolecular hydrogen-bond interactions in L-PCA crystal.

The intermolecular stabilization energy (ΔE) is defined as the difference between the total energy of a cluster of hydrogen-bonded molecules (E(cluster)) and the energy summation of separate molecules in the cluster ($\sum E$(isolated)):

$$\Delta E=E(\text{cluster})-\sum E(\text{isolated}). \quad (4)$$

Here, the ab initio calculations have been carried out by GAUSSIAN 92 program[22] packages on the IBM/RSC 6000 computer system.

Geometrical parameters of L-PCA clusters were taken from the crystallographic data as described in Ref. 13. Since there are three L-PCA molecules in the asymmetric unit, two kinds of hydrogen bonds such as [O(3)]···[H(O1)] and [H(N)]···[O(2)] are further classified into two types, resulting in the following four types A—D; (A) $[O(3)]_{2'}\cdots[H\text{–}O(1)]_3$ where the subscript m refers to the molecule m, and molecule m' is a symmetric counterpart of molecule m, (B) $[O(3)]_1\cdots[H\text{–}O(1)]_{1'}$, (C) $[H(N)]_3\cdots[O(2)]_2$, and (D) $[H(N)]_1\cdots[O(2)]_2$ (Fig. 3). These are hereinafter abbreviated as H-bond A, B, C, and D, respectively. In the case of H-bond A, B, and C, adjacent molecules are linked by a simple hydrogen bond: for example, molecules 2′ and 3 are connected by a H-bond A in Fig. 3(a) and (b). On the other hand, in the case of H-bond D, molecules 1 and 2 are linked by

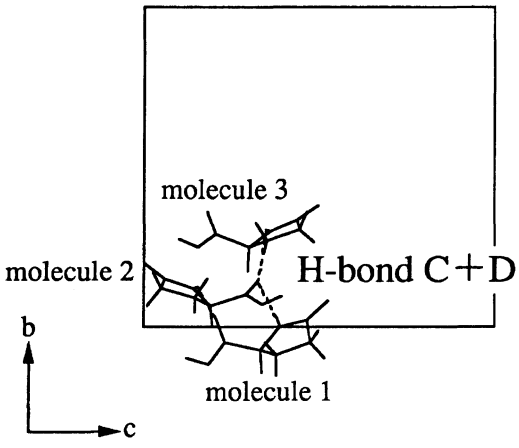

Fig. 4. Hydrogen bonds [H(N)]···[O(2)] (H-bond C+D). The hydrogen bonds are represented by broken lines (These crystal structure data are taken from the Cambridge Structural Database System (Ref. 28)).

Table 1. Calculated β Values (10^{-30} esu) for Three Asymmetric L-PCA Molecules Based on the CNDO/S-SECI and CNDO/S-CHF Method

β	Molecule 1		Molecule 2		Molecule 3	
	SECI	CHF	SECI	CHF	SECI	CHF
β_{total}	0.264	0.288	0.246	0.266	0.320	0.313
β_M	−0.172	−0.188	−0.152	−0.164	−0.175	−0.171
β_{XYZ}	0.032	0.030	0.015	0.014	0.017	0.022
β_{YZX}	0.028	0.030	0.012	0.014	0.014	0.022
β_{ZXY}	0.032	0.030	0.017	0.014	0.019	0.022

two hydrogen bonds as shown in Fig. 3(c). In addition, the cluster of molecules 1, 2, and 3 as shown in Fig. 4 including the two types of [H(N)]···[O(2)] hydrogen bonds together (H-bond C and D) should be assessed by the calculation.

The $\Delta\beta$ Values of L-PCA Clusters. The CNDO/S-SECI method have been remarkably successful in evaluation of β values for a single molecule. However, the reliability of this method when applied to molecular clusters will be harmed in the limited CI calculation due to the insufficiency of size-consistency. The ab initio method, which is good for evaluating the ΔE values, is formidable in the calculation of the β values for larger molecular system. On the other hand, the coupled Hartree–Fock (CHF) method is free from the problem of size-consistency and is still feasible even for larger molecular systems. In the mechanism of SHG by the Nd:YAG laser radiation (1064 nm) in L-PCA crystal the contribution of resonance effect seems unlikely because the L-PCA crystal is transparent down to 260 nm. This assumption seems to be supported also by the quantitative agreement between the static β values based on the CHF method and the frequency dispersion of β values based on CI method as shown in Table 1. Here, the CNDO/S-CHF method was done for the estimation of the hydrogen bond effect on the enhancement of β values ($\Delta\beta$) in L-PCA cluster.

The static polarizability and hyperpolarizabilities based on the CHF method are defined by the following equation for a molecular energy in the applied static electric field[23]

$$E=E(0)-\mu_i F_i-\frac{1}{2!}\alpha_{ij}F_iF_j-\frac{1}{3!}\beta_{ijk}F_iF_jF_k-\frac{1}{4!}\gamma_{ijkl}F_iF_jF_kF_l-\cdots, \quad (5)$$

where the repeated subscripts indicate summation.

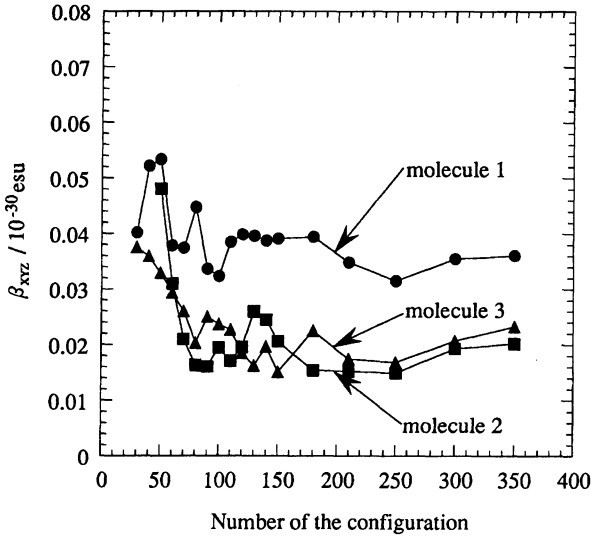

Fig. 5. Relationships between β_{XYZ} and number of the configurations. ● molecule 1, ■ molecule 2, ▲ molecule 3.

$E(0)$ is the unperturbed energy of the ground state, F_i is the electric field in the i direction, μ_i is the permanent molecular dipole moment, α is the static polarizability, and β and γ are respectively the second- and third-order static hyperpolarizabilities. In the CHF calculation the β tensors are determined from the third order numerical derivatives of the energy in terms of the applied electric fields:[24]

$$\begin{aligned}\beta_{ijk}=-\frac{1}{16F^3}[&E(F_i,F_j,F_k)-E(-F_i,F_j,F_k)\\&-E(F_i,-F_j,F_k)+E(-F_i,-F_j,F_k)\\&-E(F_i,F_j,-F_k)+E(-F_i,F_j,-F_k)\\&+E(F_i,-F_j,-F_k)-E(-F_i,-F_j,-F_k)],\end{aligned} \quad (6)$$

where $E(F_i,F_j,F_k)$ is the molecular energy under the electric field (F_i,F_j,F_k). The $\Delta\beta$ values are calculated from the difference between the β values of a cluster of hydrogen- bonded molecules (β(cluster)) and the summation of the β values of separate molecules in a cluster ($\Sigma\beta$(isolated))

$$\Delta\beta_{ijk}=\beta_{ijk}(\text{cluster})-\Sigma\beta_{ijk}(\text{isolated}). \quad (7)$$

In the similar way to the calculation of ΔE, the $\Delta\beta$ values were calculated for the clusters with four different types of hydrogen bonds, that is H-bond A, B, C, and D.

Results and Discussion

The Hyperpolarizability of L-PCA Molecule. Since there are three L-PCA molecules in the asymmetric unit and slightly differences in the conformation among the three molecules, for these three molecule 1, 2, and 3, the values of the dipole moments (μ) and the projections of the vector β onto the direction of molecular dipole moment (β_M) were calculated. In the CNDO/S-SECI calculation, although the β_M value converged with about 40 configurations, the β_{XYZ}, β_{YZX}, and β_{ZXY} values converged with about 200 configurations for these three molecules as shown in Fig. 5. Since the d_{14} ($=d_{25}=d_{36}$) value, a unique nonvanishing nonlinear coefficients in L-PCA crystal, is only dependent on those β components value, we involved 250 configurations.

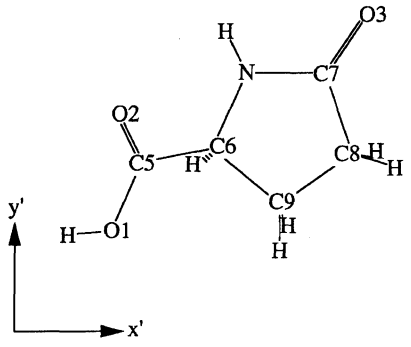

Fig. 6. The molecular coordinate system for L-PCA molecule.

Table 2. Contributed $\beta_{i'j'k'}$ Component Values (10^{-30} esu) and Its Coefficient to β_{XYZ} for three Asymmetric L-PCA Molecules

$\beta_{i'j'k'}$	Molecule 1		Molecule 2		Molecule 3	
	β Value	Coefficent	β Value	Coefficent	β Value	Coefficent
$\beta_{x'x'x'}$	0.238	0.067	0.239	0.103	0.345	0.093
$\beta_{y'y'x'}$	−0.049	−0.415	−0.073	−0.282	−0.050	−0.310
$\beta_{y'y'y'}$	0.101	0.103	0.101	0.075	0.095	0.071
$\beta_{y'z'z'}$	0.113	0.182	0.134	0.036	0.085	0.045
$\beta_{z'y'z'}$	0.114	−0.200	0.134	−0.338	0.087	−0.320
$\beta_{z'z'y'}$	0.114	−0.087	0.134	−0.048	0.087	−0.050
Approximated β_{XYZ} by above components	0.034		0.007		0.027	
Calculated β_{XYZ} by all components	0.032		0.015		0.017	

(A) Theoretical Calculation of the β Values. The calculated values of β_{XYZ}, β_{YZX}, and β_{ZXY} at the radiation energy $\hbar\omega$=1.17 eV which is corresponding to Nd:YAG laser radiation (1064 nm) are shown in Table 1. There are large differences in these values among the three molecules. Therefore, in order to investigate the molecular orientation effect on these β components among the three molecules, we picked up β_{XYZ} and tried to calculate in detail this component for each of the three molecule on the base of the molecular coordinate system (x',y',z') as shown in Fig. 6. The molecular coordinate system attached to L-PCA molecule is defined such that the molecule almost lies in $x'y'$ plane with x' axis being parallel to the amide bond (N–C(7) in Fig. 1). Then the relationship between β_{XYZ} and $\beta_{i'j'k'}$ which are the β tensor components in the principal dielectric coordinate system (X, Y, Z) and the molecular coordinate system respectively is presented as follows

$$\beta_{XYZ} = \sum_{i',j',k'} \cos\theta_{X_{i'}} \cos\theta_{Y_{j'}} \cos\theta_{Z_{k'}} \beta_{i'j'k'}, \qquad (8)$$

where $\theta_{Ii'}$ is the angle between the principal dielectric axis I and the molecular coordinate axis i'. From Eq. 8 β_{XYZ} is predominantly represented by the one by one product of $\beta_{x'x'x'}$, $\beta_{y'y'x'}$, $\beta_{y'y'y'}$, $\beta_{y'z'z'}$, $\beta_{z'y'z'}$, and $\beta_{z'z'y'}$ and the corresponding coefficients shown in Table 2. Every $\beta_{x'x'x'}$ is the primary contributor to the β_{XYZ} value for all of three asymmetric molecules and the magnitudes of the products for $\beta_{x'x'x'}$ are the molecules 3, 2, and 1 in order. However, the β_{XYZ} value of the molecule 1 is the largest value. It is due to the summation of other $\beta_{i'j'k'}$ components. For example, it can be seen that the coefficient of $\beta_{y'z'z'}$ for the molecule 1, that is the secondary contributor to the β_{XYZ} value, is largest and so on. The difference in the magnitudes of the coefficients among the three molecules is due to the difference in molecular orientation for the three molecules in L-PCA crystal rather than that of conformation in L-PCA molecule.

Table 3. Calculated Transition Energy, Transition Moment, and Dipole Moment for |1>, |2>, |3>, and |4> of L-PCA Molecules

	|1>	|2>	|3>	|4>
Transition energy (eV)	4.09	4.38	7.44	7.59
Transition moment (debye)	0.20	0.28	3.12	0.33
Dipole moment (debye)				
Excited state	4.52	4.53	10.35	6.34
Ground state	6.73	6.73	6.73	6.73

(B) Origin of the Hyperpolarizability. There is no significant difference in the calculated β_M values among the three molecules as shown in Table 1. Therefore, we examined the calculated result about the molecule 1 in order to clarify the origin of the hyperpolarizability in L-PCA molecule. Table 3 shows the calculation results for the molecule 1.

The sum-over-states expression of hyperpolarizability (Eq. 1) can be partitioned into two contributions, the two-level term (the fourth term in Eq. 1) and the three-level terms (the first, second, and third term in Eq. 1). In general, the dominant contribution to β comes from the two-level term. In the numerators of two-level terms, the primary contributors to the sum-

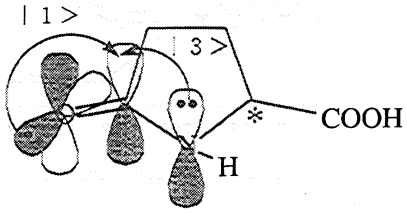

Fig. 7. Charge transfer in state 1 and 3 of L-PCA molecule.

mation come from the state which has a large transition moment ($-e \cdot r_{gn}$) and also a large difference between the ground- and excited-state dipole moments. Similarly, in terms of the denominator, when the magnitude of the transition energy between the ground and excited states ($\hbar\omega_{ng}$), is close to the value of radiation energy $\hbar\omega$ or $\hbar(2\omega)$ in the resonance sense, or the magnitude of $\hbar\omega_{ng}$ is small in the off-resonance sense, the degree of contribution to β increases. As can be seen from Table 3, |3> has the largest value in transition moment, which is over ten times larger than those of |1> or |2>, though the transition energy of |3> is only about two times larger than those of |1> or |2>. Now |3> is mainly a transition connected with the charge transfer from the n-orbital of the amide nitrogen atom to the π^*-orbital of the amide carbon atom. |1> and |2> are characterized respectively as transitions from the n-orbital of the amide oxygen atom to the π^*-orbital of the amide carbon atom, and from the π-orbital of carbon atom in the carboxyl group to the π^*-orbital of the carbonyl oxygen atom (Fig. 7). Therefore, the primary contributor to the β value is concluded to be |3>, that is, an $n_\pi \rightarrow \pi^*$ transition in the amide moiety of L-PCA molecule, which is the same origin as the case of urea.[10] This conclusion is consistent with $\beta_{x'x'x'}$ as discussed above.

Hydrogen Bond Interaction in L-PCA Crystals. (A) Intermolecular Interaction Energies. The ΔE values defined by Eq. 4 for clusters which consist of two to six L-PCA molecules connected by the H-bond A or B were obtained by use of the ab initio STO-3G calculation. In Fig. 8, the plots of ΔE for the clusters for the H-bond A and B are shown to be in linear relation with the number of molecules in clusters. Therefore, the ΔE is simply dependent on the numbers of the intermolecular hydrogen bonds and the stabilization energies per a hydrogen bond for the H-bond A and B are -7.81 and -9.14 kcal mol^{-1}, respectively. These values are equal or larger the usual hydrogen-bond energy (3—7 kcal mol^{-1}). On the other hand, the stabilization energies for the H-bond C and D are -0.82 and -1.97 kcal mol^{-1}, respectively. Since the H-bond D consist of two hydrogen bonds, one hydrogen bond [H–N]···[O(2)] contributes to the stabilization of L-PCA crystal structure as small as -0.8 to -0.9 kcal mol^{-1}. Furthermore, the ΔE of the cluster containing three molecules through the H-bond C+D is -3.50 kcal mol^{-1}, that is a minor contribution to the structural stabilization compared with that for the H-bond A or B. This can be explained by the difference in the hydrogen-bond distance; the distances of [O(3)]···[H(O1)] (H-bond A or B) and [H–N]···[O(2)] (H-bond C or D) are 1.73 and 2.30 Å, respectively. In addition, these results are also supported by the experimental observation that the cleavage planes in L-PCA crystals is the *ca* plane, perpendicular to the *b* axis which is parallel to the H-bond C and D.

(B) Influence of the Hydrogen Bond Interaction on β_{XYZ}. The influences of the hydrogen-bond interactions on the β_{XYZ} values were also investigated because the amide moiety, which is a dominant origin of β for L-PCA molecule as described previously, forms hydrogen bonds with the carboxyl and the amide moieties of the adjacent molecules as shown in Fig. 2. The $\Delta\beta_{XYZ}$ values of clusters which consist of two to six molecules connected by the H-bond A or B were obtained by use of CNDO/S-CHF calculation and Eq. 7. As shown in Fig. 9, β_{XYZ} values for the clusters forming the H-bond A and B almost are converged with three molecules in the cluster, and these are larger than the simple additivity of the three isolated molecules by 55 and 21%, respectively. For the H-bond A and B, the $\Delta\beta_{XYZ}$ values are in linear relationship with the number

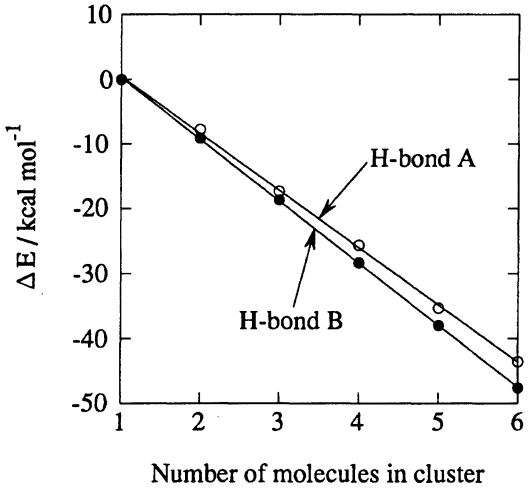

Fig. 8. Relationships between ΔE and number of molecules in cluster. ○ cluster with H-bond A, ● cluster with H-bond B.

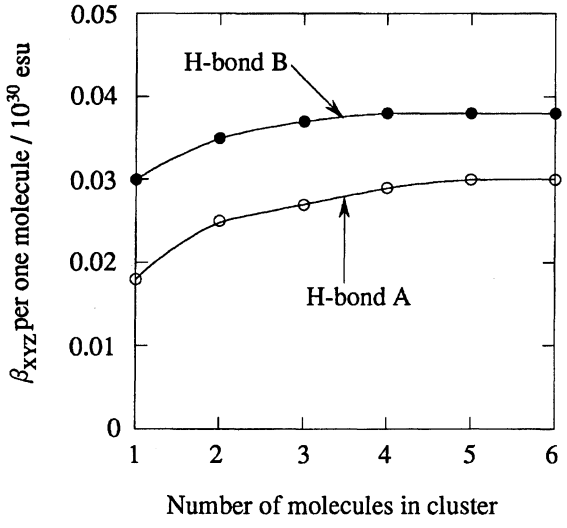

Fig. 9. Relationships between β_{XYZ} per one molecule and number of molecules in cluster. ○ cluster with H-bond A, ● cluster with H-bond B.

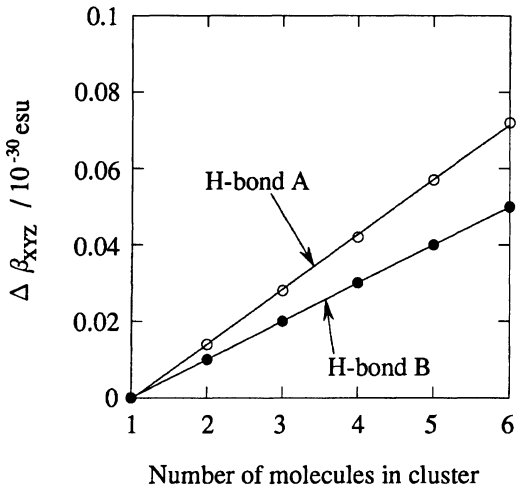

Fig. 10. Relationships between $\Delta\beta_{XYZ}$ and number of molecules in cluster. ○ cluster with H-bond A, ● cluster with H-bond B.

Table 4. The Enhancement of β_{XYZ} Value per One Molecule (10^{-30} esu) by the H-bond C and D

	β_{XYZ}(cluster)	β_{XYZ}(isolated)	The number of H-bond
H-bond C	0.020	0.018	1
H-bond D	0.032	0.026	2
H-bond C+D	0.023	0.022	3

of molecules as shown in Fig. 10. Therefore, $\Delta\beta_{XYZ}$ is simply dependent on the number of the intermolecular hydrogen bonds, similarly as in the case of ΔE. On the other hand, the β_{XYZ} values for the H-bond C+D are almost identical with the sum of the isolated molecules as shown in Table 4. Although the β_{XYZ} value for the clusters with the H-bond D alone is larger than the simple addition of the two isolated molecules by about 20%, this enhancement is canceled by the interaction of the additional H-bond C with the neighboring molecule 3. In the result, the H-bond A or B affects strongly on the π^*-orbital of the amide carbon atom, while the H-bond C or D have only a negligible influence on the n_π-orbital of the amide nitrogen atom due to the weak hydrogen bonds. Therefore, the hydrogen bonds between L-PCA molecules contribute, not only to the physical and chemical stability of L-PCA crystals, but also to the enhancement of β. The enhancement of β by hydrogen bonds has been reported also in the case of a urea crystal (β_{zzz} is increased by 70% from −44 to −74 au).[25] In both L-PCA and urea crystals the relatively large importance of intermolecular hydrogen bonds in the β enhancement is partly due to the small size of the intramolecular charge transfer in the amide moiety.

Table 5. The Variations of $\Delta\beta_{XYZ}$ Value per One Molecule (10^{-30} esu) by Each Hydrogen Bond

The number of H-bond	H-bond A	H-bond B	H-bond C+D
0	0	0	0
1	0.014	0.009	0.002
2	0.015	0.009	0.010
3	0.015	0.009	0.001
4	0.015	0.010	—
5	0.015	0.010	—

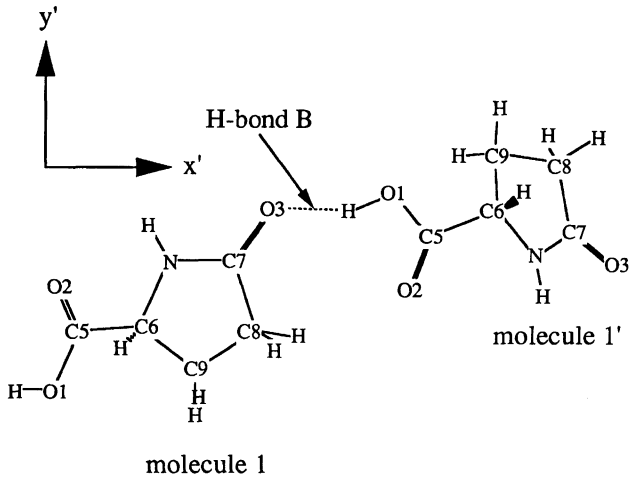

Fig. 11. The molecular coordinate system for L-PCA cluster.

By the way, the $\Delta\beta_{XYZ}$ value for the H-bond A is larger than that for H-bond B as shown in Table 5, although the two kinds of H-bonds are the same hy-

Table 6. Contributed $\Delta\beta_{i'j'k'}$ Component Values (10^{-30} esu) and Its Coefficient to $\Delta\beta_{XYZ}$ for Three Asymmetric L-PCA Molecules

$\Delta\beta_{i'j'k'}$	Molecule 1(H-bond B)		Molecule 2(H-bond A)		Molecule 3(H-bond A)	
	$\Delta\beta$ Value	Coefficient	$\Delta\beta$ Value	Coefficient	$\Delta\beta$ Value	Coefficient
$\Delta\beta_{x'x'x'}$	0.275	0.067	0.246	0.103	0.235	0.093
$\Delta\beta_{x'z'x'}$	−0.052	0.274	−0.045	0.271	−0.040	0.259
Approximated β_{XYZ} by above components	0.004		0.013		0.012	
Calculated β_{XYZ} by all components	0.009		0.014		0.014	

drogen bonds between [O(3)]···[H(O1)]. Therefore, in order to investigate this difference in the $\Delta\beta_{XYZ}$ components, we calculated in detail this components based on the molecular coordinate system (x',y',z') as shown in Fig. 6. The hydrogen bond $[O(3)]_i\cdots[H\text{–}O(1)]_j$ in the H-bond A or B in Fig. 3(a) affects $[\Delta\beta_{XYZ}]_i$ rather than $[\Delta\beta_{XYZ}]_j$, because this hydrogen bond is positional closer the amide moiety of the molecule i rather than that of molecule j. Therefore, we can assume that $[\Delta\beta_{XYZ}]_i=\Delta\beta_{XYZ}$ and $[\Delta\beta_{XYZ}]_j=0$. In the molecular coordinate system (x',y',z'), the x' axis is parallel to the amide C–N bond (C(7)–N) of the molecule i as shown in Fig. 11. From Eq. 8 $\Delta\beta_{XYZ}$ is predominantly represented by the one by one product of $\Delta\beta_{x'x'x'}$ and $\Delta\beta_{x'z'x'}$ and the corresponding coefficient that are shown in Table 6. $\Delta\beta_{x'x'x'}$ is the largest contributor to $\Delta\beta_{XYZ}$ among three asymmetric molecules. The coefficient corresponding to $\Delta\beta_{x'x'x'}$ for molecule 2 and 3 is much larger than that for molecule 1, while $\Delta\beta_{x'x'x'}$ value among the three molecules are almost equal. The difference of the values of coefficients among the three molecules can be explained by the difference of the molecular orientation in L-PCA crystal rather than that of the conformations in L-PCA molecule.

Theoretical Evaluation of the d_{14} Value in L-PCA Crystals. From the calculated values of β components, the nonlinear coefficients d_{IJK} in crystal can be estimated by the oriented-gas model[16]

$$d_{IJK}=\frac{f_I^{2\omega}f_J^{\omega}f_K^{\omega}}{V}\sum\sum(\cos{}^{(s)}\theta_{Ii})(\cos{}^{(s)}\theta_{Jj})(\cos{}^{(s)}\theta_{Kk})\beta_{ijk}^{(s)}, \tag{9}$$

where V is the unit cell volume, $f_I^{\nu}=\{(n_I^{\nu})^2+2\}/3$ is a Lorentz local field factor for the principal dielectric axis I, the frequency ν and the refractive index n_I^{ν}, θ_{Ii} is the angle between the principal dielectric axis I and the crystallographic axis i, and the summation is performed over all the molecules (indexed by s) in the unit cell. The refractive index can be calculated from the following Sellmeier's dispersion formula:[11]

$$n_X^2=2.1907+\frac{0.0142}{\lambda^2-0.0124},$$
$$n_Y^2=2.2629+\frac{0.0139}{\lambda^2-0.0148},$$
$$n_Z^2=2.5858+\frac{0.0242}{\lambda^2-0.0217}, \tag{10}$$

where λ is the wavelength in micrometers. The Sellmeier parameters were determined on the basis of the measured values of the refractive indices in the visible range (0.4—0.8 μm) and in the infrared range (1.064 μm). For the $2_12_12_1$ point group of the L-PCA crystal, there are only three nonvanishing nonlinear optical coefficients: d_{14}, d_{25}, and d_{36}.[26] When the Kleinman's symmetry relations[27] are applied, the following equality holds:

$$d_{14}=d_{25}=d_{36}. \tag{11}$$

Therefore, only d_{14}, that is d_{XYZ} in the principal dielectric coordinate system, is an independent nonvanishing tensor component. Moreover, for the $2_12_12_1$ point group, where the principal dielectric axes X, Y, and Z are found to be parallel to the crystallographic axes a, b, and c, respectively, d_{XYZ} is reduced from the Eq. 9 to the simpler form:

$$d_{XYZ}=\frac{f_X^{2\omega}f_Y^{\omega}f_Z^{\omega}}{V}\sum_s\beta_{XYZ}^{(s)}. \tag{12}$$

It is shown that the value of d_{XYZ} for L-PCA is dependent only on the β_{XYZ} value. Now, the β component values in a unit cell are expressed by the following formula

$$\beta_{ijk}=\sum\beta_{ijk}(\text{isolated})+\sum\Delta\beta_{ijk}(\text{H-bond}), \tag{13}$$

where $\sum\beta_{ijk}$(isolated) and $\sum\beta_{ijk}$(H-bond) are contributions from isolated molecules and hydrogen bond interaction, respectively, and we obtained d_{14} using Eqs. 12 and 13 for the unit cell summation as shown in Table 7. In the result it is found that the d_{14} value almost converged with the inclusion of each one of the H-bond A and B, and is estimated to be 0.30 pm V^{-1}. This value is in satisfactory agreement with the experimental results measured by the three methods: The Maker fringe method (0.22 pm V^{-1}), the phase-matching method (0.21 pm V^{-1}) and the SHG conversion efficiency (0.28 pm V^{-1}).[11]

Table 7. The Enhancement of β Values (10^{-30} esu) in a Unit Cell and d_{14} Values (pm V^{-1}) by the H-bond A and B

Number of molecules	$\Sigma\beta$(isolated)	$\Sigma\Delta\beta$(H-bond)	d_{14}
1	0.263	0	0.19
2	0.263	0.148	0.30
3	0.263	0.154	0.30
4	0.263	0.154	0.30
5	0.263	0.155	0.30
6	0.263	0.155	0.30

Conclusion

In the molecular design for second-order nonlinear optical crystals, the inclusion of hydrogen-bond interactions in crystals has been one of the effective approaches to prevent centrosymmetric packing which may otherwise occur due to the cancellation of intermolecular permanent dipole moments and as a result make SHG coefficient vanish in crystals. L-PCA molecules, novel nonlinear optical molecules, are hydrogen-bonded to form the three-dimensional network in a crystal. It has been thought that this network of hydrogen bonds influenced on the stability of the crystal structure as well as the second-order nonlinearity. From this point of view, we have performed the theoretical estimations of the contributions of the intermolecular hydrogen bonds to structural stability and second-order nonlinearity in the L-

PCA crystals by use of the molecular orbital calculation methods.

Firstly, we carried out CNDO/S-SECI calculation to understand the occurrence of the nonlinearity in L-PCA molecules. It was clear that the primary contributor to the β value is the $n_\pi \rightarrow \pi^*$ transition in the amide moiety of L-PCA molecule, as in the case of urea. The compatibility of the higher nonlinearity and the wide transparency is accomplished by the $n_\pi \rightarrow \pi^*$ transition in these molecules.

Secondly, by the ab initio STO-3G method, we calculated intermolecular stabilization energies (ΔE) of L-PCA clusters in connection by the hydrogen bonds. The calculation results indicate that the hydrogen bonds such as [O(3)]···[H(O1)] in the H-bond A and B generate large the stabilization of the crystal structure by -7.8 to -9.1 kcal mol^{-1} and thus endow the L-PCA crystal the physicochemical stability.

Thirdly, we investigated the influence of the hydrogen-bond interactions on the β_{XYZ} value by CNDO/S-CHF calculation. It was found that the large enhancement of β_{XYZ} due to the hydrogen-bond effect on the amide C–N bond, the origin of the hyperpolarizability, in L-PCA molecule: The H-bond A and B affects strongly on the π^*-orbital of the amide carbon atom.

Finally, on the basis of those calculated β components, the nonlinear coefficients d_{IJK} can be estimated by the oriented-gas model. Using the sum of the β components, including the enhancement by hydrogen bonds, of three L-PCA asymmetric molecules, we obtained $d_{14}=0.30$ pm V^{-1}. This value is in satisfactory agreement with the experimental results.

In summary, the hydrogen bonds between L-PCA molecules contribute, not only to the physical and chemical stability of L-PCA crystals, but also to the enhancement of β. The present theoretical approach to L-PCA crystal, a novel nonlinear optical material, show the benefit of hydrogen bonds in crystals concerning the structural stability and second-order nonlinearity.

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