New Crystal Form of an Organic Nonlinear Optical Material, 8-(4′-Acetylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane (APDA)

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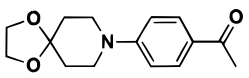
A new crystal form of an organic nonlinear optical material, 8-(4′-acetylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane (APDA) was found in the crystal growth by plate sublimation. This new crystal structure belongs to the noncentrosymmetric class, orthorhombic $P2_12_12_1$, and the unit-cell dimensions are $a = 8.428$ (8) Å, $b = 28.349$ (3) Å, $c = 5.634$ (2) Å, $V = 1346.0$ (6) Å^3, $Z = 4$, which are different from previously reported, orthorhombic $Pna2_1$. The molecule in the $P2_12_12_1$ crystal has less twisting and more bending in the structure than in $Pna2_1$. The APDA molecules are coupled in an antiparallel system in the $P2_12_12_1$ crystal as if to compensate for the repulsion arising from dipole−dipole interactions. This is in contrast to the molecular alignment of the $Pna2_1$ crystal in which the molecules are arranged in the same direction. The molecular hyperpolarizabilities (β) and d coefficients of the new crystal form were investigated theoretically by semiempirical CNDO/S-CI.

Introduction

Second-harmonic generation (SHG), which is one nonlinear optical (NLO) property, is expected for the application of frequency doublers to develop a short-wavelength laser for high-density optical data storage systems.[1] Organic materials are potential candidates for NLO owing to their large nonlinear optical susceptibilities, short response times, and high optical damage thresholds for laser power compared to the currently studied inorganic materials. Various organic materials have been investigated to be applied to NLO devices, especially frequency doublers.[2] In the course of our research, we have already found that the title compound, 8-(4′-acetylphenyl)-1,4-dioxa-8-azaspiro[4.5]decane (APDA) is an excellent NLO material for frequency



doubling. APDA single crystals of good quality and practical size for the application could be obtained from APDA melt by the Bridgman method.[3] The APDA crystal was found to possess both excellent linear and nonlinear optical properties for frequency doubling; i.e., excellent transparency down to the wavelength of 384 nm and a comparably large nonlinearity, $d_{33} = 50$ pm/V at 1064 nm.[4] Phase-matched SHG in the violet-blue region (380−450 nm) was observed from the APDA single crystal by a Ti sapphire laser pumping under collinear type I phase-matching conditions.[5] Moreover, optical flat and antireflection coated crystal surfaces were achieved,[6] and the second harmonic beam was observed at a wavelength of 405 nm from the ring resonator pumped with a laser diode.[7]

In our research and development studies regarding frequency doubling using APDA, crystal growth has been critical for nonlinear optical applications, because the crystal quality affects the efficiency of frequency conversion. To obtain APDA single crystals of good quality and practical size, we have tried to purify APDA by several methods: recrystallization from several kinds

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(1) Tatsuno, K.; Takahashi, M.; Muraoka, K.; Sugiyama, H.; Nakamura, J.; Andou, T.; Miyai, T. *Jpn. J. Appl. Phys.* **1992**, *31*, 601.

(2) (a) Chemla, D. S.; Zyss, J.; Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vols. 1 and 2. (b) Marder, S. R., Sohn, J. E., Stucky, G. D., Eds. *Materials for Nonlinear Optics: Chemical Perspectives;* ACS Symposium Series 455; American Chemical Society: Washington, DC, 1991. (c) Zyss, J., Ed. *Molecular Nonlinear Optics: Materials, Physics, and Devices;* Academic Press: Boston, 1993.

(3) Kagawa, H.; Sagawa, M.; Kakuta, A.; Kaji, M.; Nakayama, H.; Ishii, K. *J. Cryst. Growth* **1994**, *139*, 309.

(4) Sagawa, M.; Kagawa, H.; Kaji, M.; Kakuta, A. In *Electrical, Optical, and Magnetic Properties of Organic Solid State Materials*; Material Research Society: Pennsylvania, 1994; Vol. 328 of Material Research Society Symposium Proceedings; pp 601−612.

(5) Sagawa, M.; Kagawa, H.; Kaji, M.; Kakuta, A. *Appl. Phys. Lett.* **1993**, *63*, 1877.

(6) Kagawa, H.; Sagawa, M.; Kakuta, A.; Saeki, M.; Namba, Y. *Appl. Opt.* **1995**, *34*, 3421.

(7) Sagawa, M.; Kagawa, H.; Kakuta, A.; Kaji, M.; Saeki, M.; Namba, Y. *Appl. Phys. Lett.* **1995**, *66*, 547.

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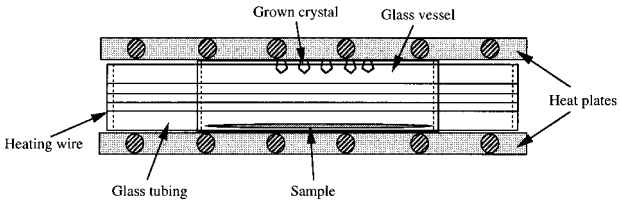


Figure 1. Plate sublimation apparatus.

of solvents, zone-refining, and sublimation. We have also applied some crystal growth methods such as melt growth (Bridgman method, Czochralski growth)[8] and solution growth with several solvents. In these trials, only one crystal form, which belongs to the noncentrosymmetric class, orthorhombic $Pna2_1$,[9] has been obtained, and crystal polymorphism, which is a well-known phenomenon in crystal growth, has not been observed. However, when we applied the plate sublimation method and analyzed the obtained crystals by X-ray diffraction, a new crystal form was found unexpectedly. We had discovered a polymorph of APDA. The existence of more than one stable or metastable crystal form is significant and interesting. In such cases, molecular packings are different, so crystal parameters, for example refractive indexes and tensor components of nonlinear optical coefficients which are very important in the design of NLO devices, are also different. Thus, there is the possibility that a suitable crystal form can be chosen, according to the type of NLO device by changing crystal growth conditions or methods. In addition, investigation of the lattice formation of the polymorph is also of value, because it may give some clues for clarification of the relationship between molecular structure and crystal structure. In this paper, we describe the molecular and crystal structures of the new crystal form as determined by X-ray crystallographic analysis. We also detail theoretical calculations of its nonlinear optical properties.

Experimental Section

Crystal Growth. Synthesis of APDA is described in ref 9. Prior to crystal growth, APDA was purified by recrystallization from ethanol followed by sublimation under reduced pressure. We used the plate sublimation method for the crystal growth. This technique was developed by Karl[10] and has proven especially suitable for the vapor growth of organic molecular crystals of good quality. This method is based on the slow sublimation of the material between two extended well-controlled isothermal plates. Therefore, the stress from the container wall and thermal decomposition of the material are reduced. The advantage of this method is that the formation of several selected seeds is possible and optically pure single crystals are obtained. The plate sublimation apparatus which was used for the crystal growth of APDA is shown in Figure 1. The purified material was enclosed in a sealed circular, cuvette-like glass vessel under a reduced pressure of 4×10^{-4} Torr. The two large circular faces of the glass vessel made contact with two larger thick metal heat plates, containing distributed heat sources and thermocouples. The glass vessel was also surrounded by a section of large diameter glass tubing and heated by a few windings of resistive wire. The material was sublimed from the lower circular face of the glass vessel to the upper face or from the upper face to the lower face. All material was transferred to the lower (upper) face by heating with the upper (lower) heating plate and ring heater. Seed formation was achieved by increasing the lower (upper) plate temperature compared to the upper (lower) one. The seed formation and crystal growth were observed directly through the ring heater and the side wall of the glass vessel. When there were too many seeds or the growing crystals were polycrystalline, all materials were transferred to the lower (upper) face again by decreasing the lower (upper) temperature. In several trials, some crystals of good quality were obtained, the sizes of which were up to 1 mm^3. Among those crystals, only one crystal was found to belong to the new crystal form. The APDA crystal which possessed the new crystal form was grown by sublimation from the upper face to the lower, the temperature of the upper heater was 107 °C and that of the lower one was 106 °C.

Table 1. Experimental Details for X-ray Measurements and Crystallographic Analysis

Data Collection

diffractometer	Rigaku AFC7R	radiation	Cu Kα
takeoff angle	6.0°	wavelength	1.54178 Å
μ	7.55 cm^{-1}	temp	293 K
abs correction	empirical (DIFABS[10])	θ range for lattice parameter	54.85° < 2θ < 56.97°
T_{max}	1.20	θ_{max}	60°
T_{min}	0.85	h	−9 → 0
collection method	$\omega-2\theta$	k	0 → 30
measd reflns	1238	l	−6 → 0
obsd reflns	1008 ($I > 3.00\sigma(I)$)		

Refinement

R	0.058	$\Delta\rho_{max}$	0.20 e $Å^{-3}$
wR	0.090	$\Delta\rho_{min}$	−0.20 e $Å^{-3}$
S	2.12	extinction correction	secondary
extinction coeff	6.3775×10^{-5}	173 parameters	
1008 reflns			

X-ray Measurements and Crystallographic Analysis. Measurements of X-ray diffraction patterns and crystallographic analysis of the new crystal form were performed by Dr. M. Shiro of Rigaku Co. Ltd., and those of the $Pna2_1$ crystal have already been reported by Ogawa et al.[9] A colorless prismatic APDA crystal having approximate dimensions of $0.35 \times 0.30 \times 0.30$ mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Cu Kα radiation. Experimental details about data collection and refinement are cited in Table 1. The structure was solved by direct methods, i.e., SHELXS86[12] and expanded using Fourier techniques, DIRDIF92.[13] Neutral atomic scattering factors were taken from *International Tables for X-ray Crystallography*, Vol IV, 2.2A.[14] All calculations were performed using the teXsan[15] crystallographic software package of Molecular Structure Corp.

Theoretical Calculation. We estimated the molecular polarizabilities (α) and hyperpolarizabilities (β) of APDA following the Ward formula, evaluating the excited states by

(8) Karl, N. In *Crystals, Growth Properties and Applications*; Freyhardt, H. C., Ed.; Springer-Verlag: Berlin, 1980; Vol. 4.
(9) Ogawa, K.; Kaji, M.; Kagawa, H.; Sagawa, M.; Kakuta, A. *Acta Crystallogr.* **1994**, *C50*, 95.
(10) Karl, N. In *Crystals, Growth Properties and Applications*; Freyhardt, H. C., Ed.; Springer-Verlag: Berlin, 1980; Vol. 4, pp 59−64.
(11) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *139*, 158.
(12) Sheldrick, G. M. In *Crystallographic Computing 3;* Sheldrick, G. M., Kruger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175−189.
(13) Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program system, Technical Report of the Crystallography Laboratory*; University of Nilmegen: Netherland, 1992.
(14) Cromer, D. T.; Waber, J. T. *International Tables for Crystallography*; The Kynoch Press: England, 1974; Vol. IV, Table 2.2A.
(15) teXsan, *Crystal structure analysis package*; Molecular Structure Corp., 1985, 1992.

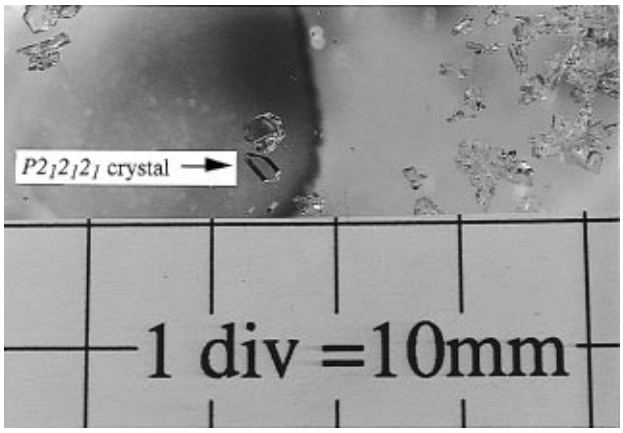


Figure 2. $P2_12_12_1$ single crystal grown by the plate sublimation.

Table 2. Crystal Data

crystal growth method	plate sublimation	from the melt and solutions
crystal system	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$Pna2_1$
a	8.428(2) Å	6.875(1) Å
b	28.349(3) Å	9.036(1) Å
c	5.634(2) Å	21.676(2) Å
V	1346.0(6) Å^3	1346.5(3) Å^3
Z	4	4
D_x	1.289 g/cm^3	1.289 g/cm^3

using the semiempirical molecular orbital, CNDO/S3-SCI.[16] The molecular axes in the hyperpolarizabilities calculations are shown in Table 5. We evaluated d coefficients of the APDA crystal in both $P2_12_12_1$ and $Pna2_1$ symmetries by using the oriented-gas model.[17] In the d coefficients calculation, we considered the Lorentz local field correction, estimating the crystal refractive indices from the molecular polarizabilities, similar to the d coefficients. As for the APDA crystal in $Pna2_1$ symmetry, the correction was performed by using not only the estimated indices but also the experimental ones.

Results and Discussion

Molecular and Crystal Structures. X-ray crystallographic analysis showed that only one crystal (Figure 2) belonged to the $P2_12_12_1$ space group and all other crystals were the usual $Pna2_1$. Crystal data of both the $Pna2_1$ and $P2_12_12_1$ crystals are shown in Table 2. Fractional atomic coordinates and selected geometric parameters of molecules in the $Pna2_1$ crystal and the $P2_12_12_1$ crystal are listed in Tables 3 and 4, respectively. The molecular structure in the $P2_12_12_1$ crystal is shown in Figure 3. All bond lengths and angles of molecules in both crystal systems are normal. Both N atoms have pyramidal geometry, and the piperidine rings adopt chair conformations. The dihedral angles between the least-squares plane of the acetyl group and that of the benzene ring deviate slightly from 0°, 5.6° in $Pna2_1$ and 2.8° in $P2_12_12_1$. Both piperidine rings have chair conformations. In the $Pna2_1$ crystal, the dihedral angle between the benzene ring and the least-squares plane of the piperidine ring is −26.6°. On the other hand, in the new crystal form, they are less twisted, and the dihedral angle is 9.9°. The bond angles of the piperidine ring are also interesting. The angles C1−N1−C13, C1−N1−C9, C11−C10−C9, and C11−C12−C13 of a $P2_12_12_1$ molecule are smaller than those of $Pna2_1$ from 0.8° to 2.0°. The bond angles N1−C9−C10 and N1−C13−C12 of a $P2_12_12_1$ molecule are larger than those of a $Pna2_1$ one by 1.8° and 2.9°. From these differences in the molecular structure, the molecule in the $P2_12_12_1$ crystal can be said to have a less twisted and more bent

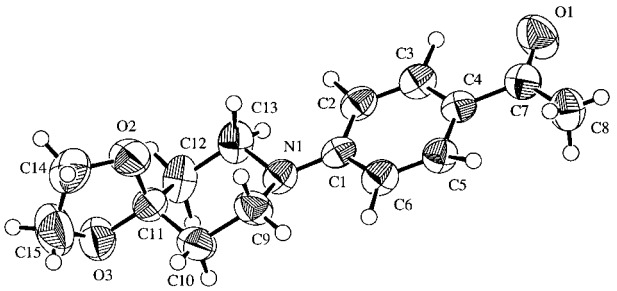


Figure 3. Molecular structure and numbering of APDA in $P2_12_12_1$ crystal.

Table 3. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters (Å^2)

$$B_{eq} = {}^8/_3\pi^2\sum_i\sum_j U_{ij}a_i^*a_j^*a_ia_j$$

	x/a	y/b	z/c	B_{eq}
O(1)	−0.0859(5)	1.1184(1)	0.2292(8)	7.6(1)
O(2)	0.1052(4)	0.7936(1)	0.1734(7)	6.61(10)
O(3)	0.3149(4)	0.7658(1)	0.3806(7)	6.69(9)
N(1)	0.1374(4)	0.9053(1)	0.4038(6)	4.54(8)
C(1)	0.0706(5)	0.9503(1)	0.3988(7)	3.97(9)
C(2)	0.1093(5)	0.9828(2)	0.2204(8)	4.74(10)
C(3)	0.0463(5)	1.0278(2)	0.2225(8)	4.7(1)
C(4)	−0.0528(5)	1.0425(1)	0.3974(8)	4.10(9)
C(5)	−0.0941(5)	1.0110(2)	0.5762(8)	4.8(1)
C(6)	−0.0318(6)	0.9653(2)	0.5734(8)	4.83(10)
C(7)	−0.1180(6)	1.0929(2)	0.3932(10)	5.0(1)
C(8)	−0.2266(6)	1.1075(2)	0.585(1)	6.0(1)
C(9)	0.0475(6)	0.8682(2)	0.5236(9)	5.4(1)
C(10)	0.1428(7)	0.8238(2)	0.5655(9)	6.0(1)
C(11)	0.2206(5)	0.8065(2)	0.3391(9)	4.85(10)
C(12)	0.3241(5)	0.8457(2)	0.241(1)	5.8(1)
C(13)	0.2254(6)	0.8894(2)	0.193(1)	5.6(1)
C(14)	0.1000(8)	0.7442(2)	0.160(1)	7.5(2)
C(15)	0.2224(10)	0.7272(2)	0.327(2)	9.5(2)

Table 4. Selected Geometric Parameters

	in $P2_12_12_1$ crystal	in $Pna2_1$ crystal
Bond Lengths (Å)		
O(2)−C(11)	1.396(6)	1.42(1)
O(3)−C(11)	1.418(6)	1.431(6)
C(10)−C(11)	1.516(7)	1.52(1)
C(11)−C(12)	1.517(7)	1.507(7)
N(1)−C(1)	1.395(6)	1.38(1)
C(4)−C(7)	1.507(7)	1.48(1)
O(1)−C(7)	1.220(6)	1.21(1)
Bond Angles (deg)		
O(2)−C(11)−O(3)	106.8(3)	106.5(7)
C(10)−C(11)−C(12)	108.5(4)	110.4(7)
C(9)−N(1)−C(13)	114.4(4)	112.0(7)
C(1)−N(1)−C(9)	117.3(4)	119.3(5)
C(1)−N(1)−C(13)	117.9(3)	119.1(9)
O(1)−C(7)−C(4)	120.2(5)	120.7(6)
Torsion Angles (deg)		
O(2)−C(11)−C(10)−C(9)	−63.8(5)	−173.0(4)
O(3)−C(11)−C(12)−C(13)	179.5(4)	69(1)
O(3)−C(11)−C(10)−C(9)	177.8(4)	70.5(6)
C(2)−C(1)−N(1)−C(13)	−11.6(6)	44.2(7)
C(6)−C(1)−N(1)−C(9)	27.7(6)	4.5(9)
C(3)−C(4)−C(7)−C(8)	179.8(4)	−176.8(8)
O(1)−C(7)−C(4)−C(3)	2.2(7)	−4(1)

(16) Lalama, S. J.; Garito, A. F. *Phys. Rev. A* **1979**, *20*, 1179.
(17) Chemla, D. S.; Oudar, J. L.; Jerpfagnon, J. *Phys. Rev. B* **1975**, *12*, 4534.

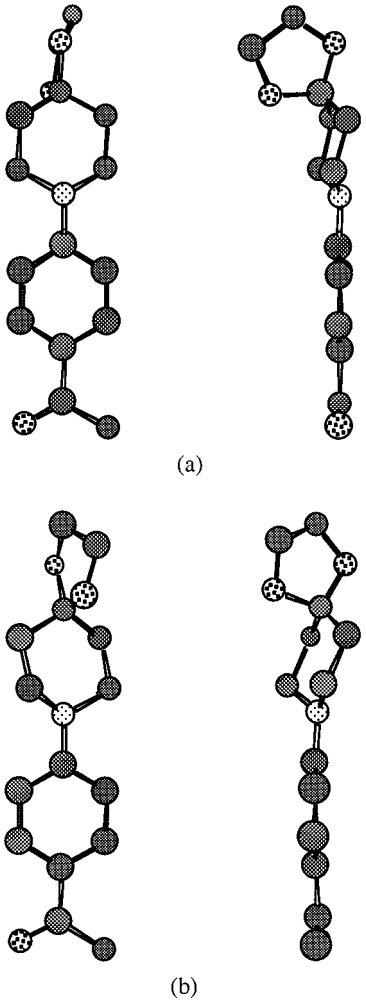


Figure 4. Molecular structures in both (a) the $P2_12_12_1$ and (b) the $Pna2_1$ crystal.

structure than that of the $Pna2_1$ crystal (Figure 4). The molecular conformations are slightly different in different states of aggregation.

Differences between the two crystal structures are more notable. In the new crystal form, $P2_12_12_1$, molecules are aligned antiparallel along the crystallographic *b* axis so that the electrostatic repulsion between the largest dipole moments parallel to the longest molecular axis may be compensated (Figure 5). On the contrary, despite electrostatic repulsions due to dipole−dipole interactions, APDA molecules in the $Pna2_1$ crystal are arranged in the same direction, and the longest molecular axis is along the crystallographic *c* axis (Figure 6). In the case of APDA, formations of intra- and intermolecular hydrogen-bonding and charge-transfer complexes, which strongly affect the crystal lattice formation, are not expected to contribute, because APDA has no such functional groups and structure. It can be assumed from molecular packing that when a $P2_12_12_1$ crystal is growing, intermolecular dipole−dipole interactions mainly affect the crystal formation and reduce the electrostatic repulsions. The X-ray diffraction pattern showed that the usual "rough" sublimation gives only the $Pna2_1$ crystal form and that other crystals obtained from the plate sublimation also had the $Pna2_1$ form. Thus, the starting APDA in the glass vessel in this plate sublimation growth must have the $Pna2_1$ form. In addition, a $Pna2_1$ crystal does not change its form to $P2_12_12_1$ thermally. If APDA molecules sublime

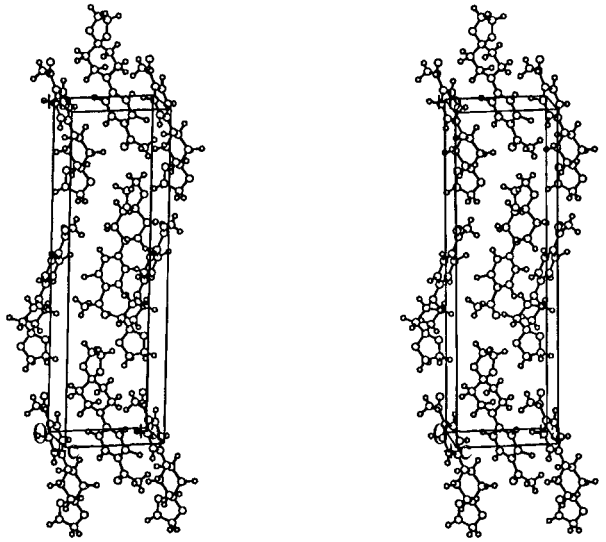


Figure 5. Stereoscopic view of a unit cell of the $P2_12_12_1$ crystal.

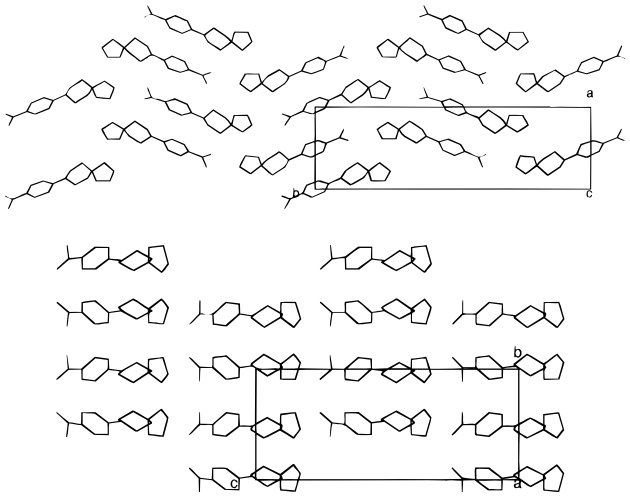
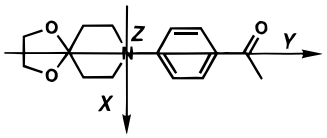


Figure 6. Schematic drawings of (a, top) $P2_12_12_1$ and (b, bottom) $Pna2_1$ crystal structures.

maintaining the $Pna2_1$ alignment, grown crystals will have the $Pna2_1$ form. Hence, to form the $P2_12_12_1$ crystal, the APDA molecule should sublime from the $Pna2_1$ crystal as a unimolecule. In our plate sublimation experiment, the sublimation conditions which form $P2_12_12_1$ crystals may have been achieved by the extremely low growing rate and pressure, so one $P2_12_12_1$ crystal could be obtained. If a crystal growth method which works by such conditions, for example the molecular beam epitaxy (MBE), is applied to APDA, the $P2_12_12_1$ crystal form is assumed to be also obtained.

$P2_12_12_1$ crystals have not been obtained from the melt nor from several types of solvents, for example, ethanol, ethyl acetate, acetonitrile, acetone, and toluene. In addition, $P2_12_12_1$ crystals were not always obtained from vapor. We have tried to grow $P2_12_12_1$ crystals for other measurements by plate sublimation in many times, but only one crystal has been obtained. Moreover, due to the electrostatic interaction between molecules, the $P2_12_12_1$ crystal form is expected to be more stable than the $Pna2_1$ crystal. However, the $Pna2_1$ crystal shows only one phase transition which is at its melting point. No other transitions corresponding to a change in crystal form, i.e., from $Pna2_1$ to $P2_12_12_1$ have been

Table 5. Calculated β Values of APDA (10^{-32} esu)[a]



component	$P2_12_12_1$ APDA	$Pna2_1$ APDA
β_{xxx}	−0.54	−0.47
β_{xyy}	0.17	1.1
β_{xzz}	−0.0013	0.0017
β_{yyy}	2.7	6.1
β_{yxx}	−0.77	−1.3
β_{yzz}	0.0013	0.0011
β_{xxz}	0.46	0.026
β_{yyz}	−0.057	0.19
β_{zzz}	0.00019	−0.000013

[a] The origin is located on the N atom. The *Z* axis is out of the plane of the paper.

observed by differential scanning calorimetry. The dipole moments were calculated based on the molecular structures obtained from X-ray crystallographic analysis. The dipole moment of the $Pna2_1$ molecule along the longest molecular axis is calculated as 6.7 D, and the dipole moment of $P2_12_12_1$ is calculated as 5.9 D. Explaining the crystal formation based on the molecular structure in the crystal state is not always valid, because the molecular structure in the gas phase is not always the same as in the solid phase. It is reported that the torsion angle for biphenyl is about 40° in the vapor phase,[18] while the molecule is planar in the solid state. However, judging from the calculated dipole moments based on the molecular structures in the crystal states, the difference in molecular arrangements of the two crystal forms cannot be explained only from the dipole−dipole interactions. A $Pna2_1$ crystal was confirmed to grow from the melt along the crystallographic *a* axis (which is out of the plane of the paper in Figure 6b). Thus, if the dipole−dipole interactions would have an important effect upon crystal growth, antiparallel arrangement might be introduced, but it was not. Namely, the primary factor which determines the structure of the $Pna2_1$ crystal should be expected to be something other than dipole−dipole interactions. Weissbuch et al.[19] proposed that in supersaturated solutions molecules assemble to form coexisting ordered clusters of structures resembling the crystals into which they eventually develop. Weissbuch's group is attempting to control crystal polymorphism with the assistance of nucleation inhibitors along this working hypothesis. We think that the effect of neighboring molecules on a depositing APDA molecule should also be taken into account, for example solvation or the solvated molecule or molecular aggregation.

Nonlinear Optical Property. A relationship between polymorphism and nonlinear optical properties has been reported by Hall et al.[20] They discussed the relationship between crystal forms and the intensities of the second harmonic beams generated from powder samples. However, the powder technique[21] is just a qualitative measurement, and the intensity of the second harmonic beam is affected by the size and shape of the particles in the powder. In addition, only a second harmonic signal which depends on phase-matchable tensor components of d_{ij} coefficients can be detected. Therefore, molecular hyperpolarizability (β) and *d* coefficients were calculated theoretically. β values calculated by the CNDO/S3-SCI method are tabulated in Table 5. In both crystal structures, β_{yyy} ($=\beta_{ct}$) which is due to the donor−acceptor charge transfer has the largest value. The β_{yyy} value of the molecule in $P2_12_12_1$ crystal is smaller than that of $Pna2_1$.

The β_{yyy} is expressed by a two-level approximation[22] as in

$$\beta_{ct} = \frac{3e^2\hbar^2}{2m}\frac{W}{[W^2-(2hw)^2][\Omega^2-(\hbar w)^2]}f\Delta\mu_{ex}$$

In eq 1, $\Delta\mu_{ex}$ is the difference between the first excited- and the ground-state dipole moments, *f* is the oscillator strength for the transition, and *W* is the energy difference between the excited and the ground states. The molecules which are more planar in structure (which have donor−[π-electron system]−acceptor systems) also have larger β_{ct} values. In these molecules, the overlapping between π-electron orbitals may effectively contribute to enhance intramolecular charge transfer, and the energy differences between the excited state and the ground state (*W*) are reduced as a result. In the case of APDA, the $P2_12_12_1$ molecule which has a smaller β_{yyy}, has a less twisted and more bend structure than a $Pna2_1$ molecule. On the basis of only on these results, bending seems to have more effect than twisting on β_{ct} of the APDA molecule. This may mean that the bending deformation affects the overlapping between the π-electron orbitals. We will investigate the relationship between these structural differences and the terms in eq 1 and report the results elsewhere.

The APDA crystal symmetry belongs to a point group *222*, so the tensor of its nonlinear optical coefficients d_{ij} is given by

$$d = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & d_{36} \end{pmatrix}$$

The tensor components were theoretically calculated based on the oriented gas model (Table 6) by using calculated values of the refractive indexes and β values. In the case of $Pna2_1$, large enough single crystals could be grown to measure their optical properties, and the calculated values of d_{ij} using measured values of the refractive indexes are also listed in the table. The largest values of d_{ij} were $d_{36} = 6.7$ pm/V in $P2_12_12_1$ and $d_{33} = 15$ pm/V in $Pna2_1$. In the case of the $Pna2_1$ crystal, the calculated d_{ij} values using the measured refractive indexes ($d_{33} = 61$ pm/V, $d_{32} = 8.7$ pm/V) are almost 3−4 times larger than the calculated values by using the calculated refractive indexes ($d_{33} = 15$ pm/V, $d_{32} = 2.9$ pm/V), and they agree well with the measured values, $d_{33} = 50$ pm/V and $d_{32} = 7$ pm/V obtained by

(18) Almenningen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. *J. Mol. Struct.* **1985**, *128*, 59.
(19) (a) Weissbuch, I.; Addadi, L.; Lahav, M.; Leiserowitz, L. *Science* **1991**, *253*, 637. (b) Lahav, M.; Leiserowitz, L. *J. Phys. D* **1993**, *26*, B22. (c) Weissbuch, I.; Leiserowitz, L.; Lahav, M. *Adv. Mater.* **1994**, *6*, 952.
(20) Hall, S. R.; Kolinsky, P. V.; Jones, R.; Allen, S.; Gordon, P.; Bothwell, B.; Bloor, D.; Norman, P. A.; Hursthouse, M.; Karaulov, A.; Baldwin, J.; Goodyear, M.; Bishop, D. *J. Cryst. Growth* **1986**, *79*, 745.
(21) Kurtz, S. K.; Perry, T. T. *J. Appl. Phys.* **1968**, *39*, 3789.
(22) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

Table 6. Calculated d_{ij} Coefficients

form	calcd d_{ij} coefficients (pm/V) with calculated refractive indexes	calcd d_{ij} coefficients (pm/V) with measured refractive indexes
$P2_12_12_1$	$\begin{pmatrix} 0 & 0 & 0 & 6.5 & 0 & 0 \\ 0 & 0 & 0 & 0 & 5.8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 6.7 \end{pmatrix}$	
$Pna2_1$	$\begin{pmatrix} 0 & 0 & 0 & 0 & 5.53 & 0 \\ 0 & 0 & 0 & 2.90 & 0 & 0 \\ 6.00 & 2.92 & 15.4 & 0 & 0 & 0 \end{pmatrix}$	$\begin{pmatrix} 0 & 0 & 0 & 0 & 17.4 & 0 \\ 0 & 0 & 0 & 8.50 & 0 & 0 \\ 19.0 & 8.74 & 60.8 & 0 & 0 & 0 \end{pmatrix}$

the Maker fringe method. From these results, the d coefficients of $P2_12_12_1$ are also estimated at 3−4 times larger than the calculated values, and d_{36} is about 20 pm/V. This value is one-tenth of the d_{11} coefficient of 2-methyl-4-nitroaniline (MNA).[23] To measure the nonlinear optical coefficients d_{ij} quantitatively, the Maker fringe method[24] should be applied to the crystals. However, we have succeeded in growing a small $P2_12_12_1$ crystal only once. If $P2_12_12_1$ crystals are obtained, we tried to grow large crystals from the melt or the solution which are enough to be measured by the Maker fringe method.

Conclusions

A new crystal form of an organic nonlinear optical material, APDA, was found. The crystal was grown by the plate sublimation method. The crystal structure was analyzed by X-ray crystallographic analysis. It belongs to the noncentrosymmetric class, orthorhombic $P2_12_12_1$, and the unit-cell dimensions are $a = 8.428$ (8) Å, $b = 28.349$ (3) Å, $c = 5.634$ (2) Å, $V = 1346.0$ (6) Å^3, $Z = 4$, which differ from the previously obtained crystal, orthorhombic $Pna2_1$. The molecule in the $P2_12_12_1$ crystal has a less twisted and more bend structure than $Pna2_1$ does. In the $Pna2_1$ crystal, APDA molecules are arranged in the same direction. By contrast, in the new crystal form $P2_12_12_1$, the molecules are arranged in an antiparallel system as if to reduce the electrostatic repulsions which arise between the largest dipole moment parallel to the longest molecular axis. It can be assumed from such molecular packing that the intramolecular dipole−dipole interactions mainly affect the $P2_12_12_1$ crystal lattice formation. With regard to the $Pna2_1$ crystals formation, other factors should be taken into account, for example effects from neighboring molecules. In such a system, the prediction of crystal structure from molecular structure[25] remains difficult. The molecular and crystal structures of some *N*-arylpiperidine derivatives will be reported elsewhere.

The nonlinear optical properties of the new crystal form were investigated by theoretical calculations. The first-order hyperpolarizability along the charge-transfer axis of the molecule in the $P2_12_12_1$ crystal is less than half of that in the $Pna2_1$ crystal. The largest value of the nonlinear optical coefficients of the new crystal was calculated as 6.7 pm/V and it is about two- or three-fifths of the d_{33} of $Pna2_1$ APDA. The new crystal form of APDA reported in this paper can give new NLO devices. Suitable crystal growth techniques should be developed for the new devices.

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Supporting Information Available: X-ray crystallographic data (8 pages); observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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(23) Lipscomb, G. F.; Garito, A. F.; Narang, R. S. *J. Chem. Phys.* **1981**, *75*, 1509.
(24) Maker, P. D.; Terhune, R. W. *Phys. Rev. Lett.* **1962**, *8*, 21.
(25) Gavezzotti, A. *Acc. Chem. Res.* **1994**, *27*, 309.