of $H_2PtCl_6$ by citrate in water.[22] As shown in Figure 8, the white-line intensity of the aqueous platinum colloid was significantly greater than that for colloid **2**. The differences in white-line intensities and curve shapes demonstrated that colloid **2** has a different structure and was more reduced than the aqueous platinum colloid.

Analysis of the specific identity of the surface ligands of the Pt, Rh, and Pd colloids in this work awaits study by EXAFS. It is well-known for Pt and Rh that in the presence of terminal olefins, $R_3SiH$ is cleanly added intact to the olefin in the presence of the metal. Very little olefin hydrogenation occurs in these systems, and no example of disilane addition has been reported; thus the surface of the colloid may be composed of $R_3Si$ fragments and H. Indeed all of the X-ray spectroscopic analyses we have made of the dark spots (colloids) show metal, silicon, and oxygen; however, further work is needed to determine the exact nature of the surface species.

The structure of the Ru, Os, and Ir materials is more speculative. A number of workers have discussed the problem of the boundary between authentic large molecular clusters and colloids.[23] In one study, a cluster as small as $Os_{10}$ has been shown to possess significant bulk metal properties.[24] The cluster containing $Au_{18}Ag_{20}$ has a diameter of 1.5 nm and likewise shows evidence of significant metal-band-like characteristics.[25] The Ru, Os, and Ir materials prepared here no doubt lie on the boundary of cluster and colloid, stabilized by silicon species.

This report describes a straightforward method for preparation of metal colloids in low dielectric constant media. Due to the high surface area the obvious use for the materials is in the area of catalysis.[8] As shown by the TEM/HREM analyses, it is possible to deposit the metal crystallites intact; thus these colloidal mixtures may have application for deposition of metals onto a variety of substrates.

**Acknowledgment.** Dr. Ernie Hall carried out the HREM measurements, Dr. Mike Burell and Mr. John Chera performed the ESCA analyses, Dr. Elizabeth Williams, Paul Donahue, and Joanne Smith carried out some of the NMR measurements and participated in helpful discussions, Winnie Balz carried out the ICP metal analyses, and Dr. Pete Codella carried out the Raman measurements. Professor Robert Crabtree, Yale University, is acknowledged for providing some key references and for valuable discussions. Dr. Joe Wong, Livermore National Laboratory, assisted in the XANES measurements and analyses.

**Supplementary Material Available:** AEM for Rh colloid (eq 3), HREM for Os colloid, HREM for Ru colloid, XANES spectra for various Pt colloids; all photomicrographs (6 pages). Ordering information is given on any current masthead page.

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# Centrosymmetric Crystals as Host Matrices for Second-Order Optical Nonlinear Effects†

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Reduction of crystal symmetry via preferential occlusion of guest molecules through different subsets of crystal surface sites has been used to include centrosymmetric host crystals as a matrix for providing second-order nonlinear optical effects. The method is also applicable for generating a second harmonic signal along the principal nonpolar axis of polar crystals. This approach is illustrated by several examples. These optical measurements yield information on crystal growth processes and on the alignment of guest molecules in the host crystal.

Recent studies have revealed large molecular hyperpolarizabilities $\beta$ of certain organic materials, leading to anomalously large optical nonlinearities relative to those of more conventional inorganic substances.[1-3] Second-order optical effects, such as second harmonic generation (SHG), optical rectification, sum and difference frequency mixing, and parametric generation or amplification by three-photon interactions, are all governed by a third-rank tensor.[4] Thus, to be potentially useful for these effects,

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† Part of this work was done during a sabbatical leave of M.L. and L.L. in the laboratory of Dr. E. Wassermann, Du Pont.

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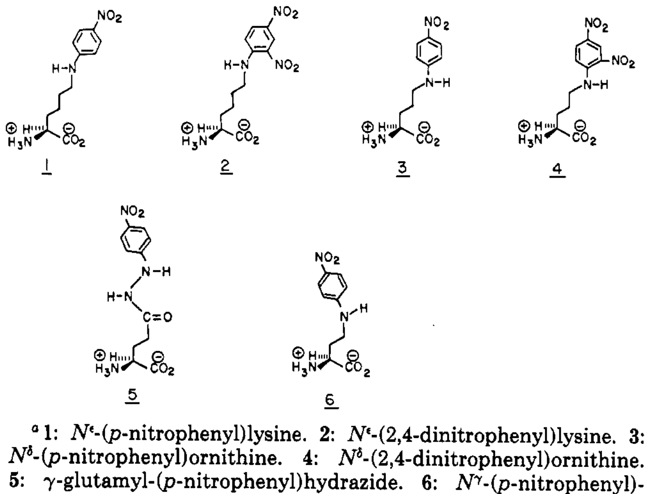
**Chart I. Representation of the α-Amino Acids Used as Guest Molecules in Various Host Matrices**[a]



[a] 1: $N^{\epsilon}$-(*p*-nitrophenyl)lysine. 2: $N^{\epsilon}$-(2,4-dinitrophenyl)lysine. 3: $N^{\delta}$-(*p*-nitrophenyl)ornithine. 4: $N^{\delta}$-(2,4-dinitrophenyl)ornithine. 5: γ-glutamyl-(*p*-nitrophenyl)hydrazide. 6: $N^{\gamma}$-(*p*-nitrophenyl)-α,γ-diaminobutyric acid.

the material must be acentric.[5] In addition, for SHG and those processes for which the Kleinman symmetry holds, the acentric crystal class 432 is also forbidden.[6] However, the overriding majority of organic materials appear in centrosymmetric crystal structures. Several different methods have been used to induce the crystallization in a noncentrosymmetric arrangement. One obvious way is to attach a chiral handle to the molecule. Another method is to crystallize the molecules in a chiral inclusion complex.[7,8] Recently, the use of polar solvents to induce crystallization in a noncentrosymmetric polymorph has also been reported.[9]

Here we present a method that can considerably ease the above stringent selection rules by rendering centrosymmetric materials useful as host matrices for second-order nonlinear effects. We also demonstrate that SHG and related second-order processes are excellent analytical tools to study material structural properties for which other more conventional diagnostic methods are insensitive. The principles of this new method are explained and illustrated with a few examples.

Recently, it was shown that adsorption and occlusion of minor amounts of additive during growth of crystalline solid solutions is dictated by the symmetry and structure of the crystal surfaces through which the additive molecules are occluded.[10] It was demonstrated that the guest molecules may be adsorbed and preferentially occluded through different subsets of surface sites on the crystallographically different faces, leading to a mixed crystal of sectors of reduced symmetry, coherently compounded together.[11,12] In this way it was possible to induce guest molecules to be aligned in a polar arrangement within a nonpolar crystal, making the latter susceptible to otherwise forbidden second-order optical nonlinearities. Here we report successful SHG studies on two host–guest mixed crystals where the occluded guest molecules have indeed induced a loss of the crystallographic center of symmetry by virtue of being arranged in a polar manner in the "centrosymmetric" host matrix. First, the potential of the method is demonstrated with centrosymmetric host crystals of *p*-(*N*-dimethylamino)benzylidene-*p*′-nitroaniline, which become acentric upon occlusion of the quasi-centrosymmetric guest molecule *p*,*p*′-dinitrobenzylideneaniline. Second, we report on crystals of α-glycine, centrosymmetric in its pure form, which show SHG upon occlusion of α-amino acids bearing the *p*-nitroaniline moiety (see Chart I, compounds **1**, **3**, and **6**). By a similar approach we have obtained SHG along the three principal axes of the mixed crystals of (*S*)-glutamic acid·HCl with α-amino acids **1**–**6**. The pure host counterpart is acentric (space group $P2_12_12_1$) but with SHG symmetry forbidden along the principal axes. The appearance of SHG along these directions in the mixed crystal therefore is indicative of the reduction of symmetry down to the triclinic space group $P1$. To emphasize the strength of the method from the standpoint of molecular engineering, it is shown that even minimal amounts of additive (e.g., 0.01 wt %) can lead to substantial SHG signals. Equally important, we also demonstrate that SHG measurements on these systems, contrary to more conventional techniques, can allow one to study the orientation of the guest molecules occluded inside the host matrix, even at these small concentration levels.

For the experiments we utilized a continuous mode-locked Nd:YLF laser emitting 35-ps pulses at a repetition rate of 100 MHz. This system has been described elsewhere.[13] The average output power at 1.053 μm is continuously variable from 0 to 10 W. The Gaussian laser beam is linearly polarized, with a provision for rotating the polarization over 360°. The beam is weakly focused into the samples to a spot size of 120 μm to make the Rayleigh range much larger than the sample thickness. All samples are mounted on a goniometer head to permit accurate alignment of the fundamental beam along a crystallographic axis. The harmonic radiation from the samples is synchronously detected with a lock-in amplifier through a high *f* number, spectrally filtered, high-efficiency collection system. Thus, a strong discrimination against incoherent emission and scattered light is achieved. The polarization of the second harmonic radiation is measured with a polarizer-analyzer. Calibration of the SHG signals is obtained relative to crystalline quartz. The high sensitivity of the apparatus allows one to detect SHG signals more than 4 orders of magnitude weaker than those obtained from quartz.

We now discuss the experimental results for three of the mixed systems that we have studied so far.

***p*-(*N*-Dimethylamino)benzylidene-*p*′-nitroaniline.** To demonstrate the principle of reduction of symmetry, we used as host the crystal of *p*-(*N*-dimethylamino)benzylidene-*p*′-nitroaniline, which, when pure, is centrosymmetric and composed of molecules with a high β coefficient. The guest molecule, *p*,*p*′-dinitrobenzylideneaniline, is essentially centrosymmetric. The pure crystals are orange {010} plates of symmetry $P\bar{1}$, polymorph II.[14] We could not obtain pure crystals of polymorph I,[15] also

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(4) See, e.g.: Shen, Y. R. *The Principles of Nonlinear Optics*; Wiley: New York 1984. See also: Zernike, F.; Midwinter, J. E. *Applied Nonlinear Optics*; Wiley: New York, 1973.

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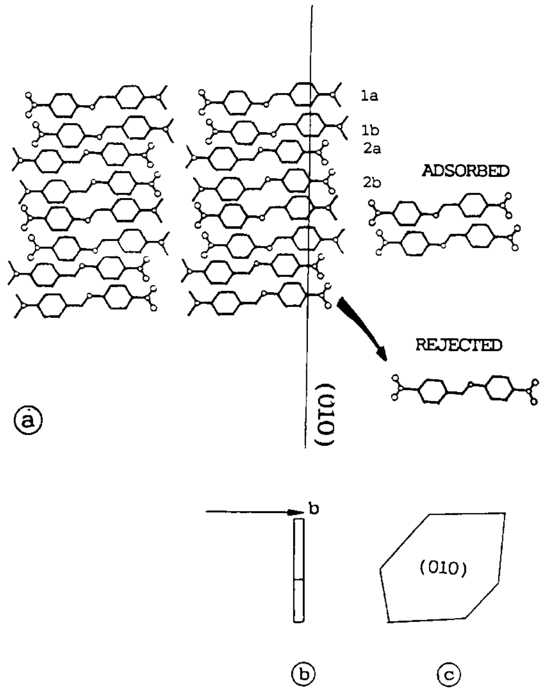

**Figure 1.** (a) Packing arrangement of the *p*-(*N*-dimethylamino)benzylidene-*p*′-nitroaniline crystal polymorph II, along the *b* axis viewed edge on. Schematic morphology of the crystals: (b) (010) face viewed edge on; (c) (010) within the plane of the paper. 1a and 1b denote independent molecules that are symmetry related with the 2a and 2b molecules, respectively.

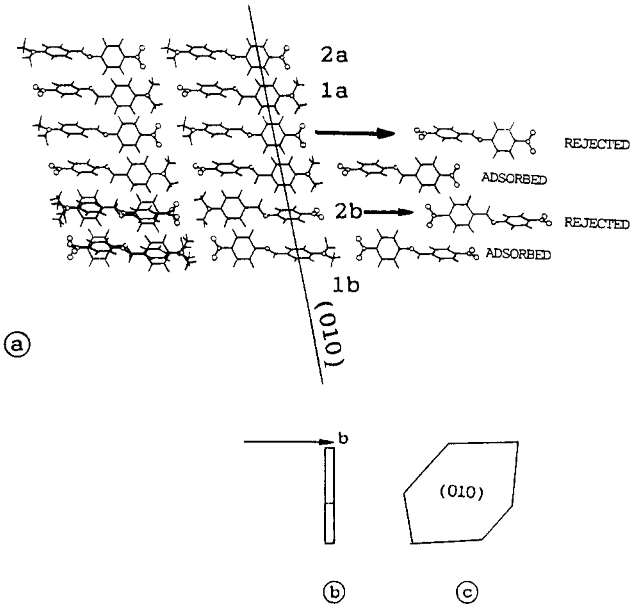

**Figure 2.** (a) Packing arrangement of the *p*-(*N*-dimethylamino)benzylidene-*p*′-nitroaniline crystal polymorph I, along the *b* axis viewed edge on. Schematic morphology of the crystals: (b) (010) face viewed edge on; (c) (010) within the plane of the paper. 1a and 1b denote independent molecules that are symmetry related with the 2a and 2b molecules, respectively.

of space group $P\bar{1}$, by crystallization from acetone. However, when grown in the presence of the additive, mixed crystals of both polymorphs, as identified by X-ray diffraction, appear in the same crystallization batch.[16] These two polymorphs exhibit similar packing arrangements but differ in their molecular conformations. According to the host crystal structures, shown in Figures 1 and 2, it is expected that a guest molecule may be preferentially adsorbed at face (010) only at molecular sites of type 1; adsorption at site 2 is unfavorable since the (methyl)C–H···O(nitro) intermolecular contacts would be replaced by N–O(guest)···O–N(host) lone pair–lone pair repulsion.[17] Thus, incorporation of guest molecules through the (010) face at sites related by translation only would yield a net dipole moment for each of the host molecules that does not have an inversion-related counterpart at the site occupied by the guest. It was verified that no SHG could be obtained from the pure crystals. On the other hand, the mixed crystals of both polymorphs indeed do frequency double, demonstrating a loss of the crystallographic center of inversion. The fundamental beam propagates along the normal to the crystal plates, giving rise to a type I SHG (polarization direction of both fundamental and second harmonic fields being parallel to the short crystallographic axis). As expected, the SHG intensity strongly varies with the concentration of the guest molecules. For mixed crystals grown from solution in the presence of a guest concentration of 10, 20, and 30 wt %, the SHG signal varied from $4 \times 10^{-5}$ to $6.5 \times 10^{-3}$ to $1.2 \times 10^{-2}$, respectively, in units relative to SHG in quartz.

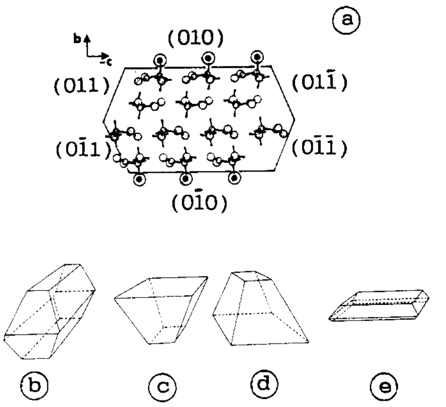

**Figure 3.** (a) Packing arrangement of the α-glycine crystal viewed along the *a* axis. Schematic morphologies of the crystals: (b) pure; (c–e) grown in the presence of *R*, *S*, *R*,*S* additives, respectively.

**Glycine.** Pure glycine crystallizes from aqueous solution in the centrosymmetric monoclinic space group $P2_1/n$ in the form of bipyramids with the *b* axis perpendicular to the basal plane of the pyramid (figure 3).[18] When the crystals are grown in the presence of any natural (*S*)-α-amino acids, there occurs a dramatic morphological change at the −*b* side, yielding pyramids with a dominant $(0\bar{1}0)$ basal face. The morphological symmetry is thus recorded from $2/m$ in the pure form to 2 in the affected crystal. All (*R*)-α-amino acids induce crystallization of the enantiomorphous pyramidal morphology with a basal (010) face. A racemic additive yields {010} crystal plates.

α-Amino acid additives were found in the bulk of the glycine crystals ranging in concentrations from 0.01 to 0.2 wt %. HPLC analysis of these α-amino acids occluded inside single platelike crystals of glycine demonstrated a total enantioselective segregation along the *b* axis; as expected, the (*R*)-α-amino acids predominated at the +*b* half

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(15) Nakai, H.; Shiro, M.; Ezumi, K.; Sakata, S.; Kubata, T. *Acta Crystallogr., Sect. B* **1976**, *32*, 1827.

(16) We assume that the presence of the additive molecules may either induce or stabilize the polymorph I.

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(18) Weissbuch, I.; Addadi, L.; Berkovitch-Yellin, Z.; Gati, E.; Weinstein, S.; Lahav, M.; Leiserowitz, L. *J. Am. Chem. Soc.* **1983**, *105*, 6613, and references therein.

of the crystal and the (*S*)-$\alpha$-amino acids at the $-b$ half.

These results demonstrate that the mixed crystal is composed of two enantiomorphous halves, unlike the centrosymmetric host crystal. In each half there is a loss of the overall inversion symmetry since the additive molecules can be adsorbed at only a subset of {010} surface sites related by symmetry elements of the first kind. We undertook a SHG study on these mixed $\alpha$-glycine crystals to provide more direct information on the symmetry of the mixed crystal and on the alignment of the guest molecules.

To enhance the SHG signal, we made use of $\alpha$-amino acid guest molecules with side chains containing groups with high $\beta$ coefficients. Thus we prepared *p*-nitrophenyl derivatives of lysine, ornithine, and $\alpha,\gamma$-diaminobutyric acid (see Chart I). To obtain large {010} plates, we grew the glycine crystals at the air/solution interface from solutions containing, as additives, mixtures of the above guests of *S* configuration and (*R*)-leucine. The (*R*)-leucine induces formation of glycine crystals floating at the interface with their (010) faces exposed to the air, so that the *S* guest molecules may be occluded through the $(0\bar{1}0)$ face exposed to solution.[19] The guest molecules may be preferentially adsorbed at two of the four symmetry-related sites on the $(0\bar{1}0)$ surface, the two sites being related by 2-fold screw symmetry. Such a crystal upon guest occlusion will have ideally $P12_11$ symmetry and consequently will be SHG forbidden for a fundamental beam propagating along the *b* axis.

As expected, the pure $\alpha$-glycine crystals do not show any SHG. However, all the mixed glycine crystals give rise to relatively strong type II SHG for a fundamental beam propagating along the *b* axis. Maximum SHG in these cases is obtained for the fundamental field being polarized at 45° from the reciprocal $a^*$ and $c^*$ axes, giving rise to a second harmonic field polarized along the $c^*$ axis. These results imply that the overall symmetry of the mixed crystal structure is not $P2_1$ but $P1$. This $P1$ symmetry may be interpreted in terms of a growth mechanism of the 010 layers in the *b* direction since the guest molecule cannot be occluded at the {011} and {110} faces.[18] We will address this issue later. From the SHG intensity one can calculate a value for the effective nonlinear constant $d_{\mathrm{eff}}$. We illustrate this with an example. Glycine crystals containing $N^{\epsilon}$-(*p*-nitrophenyl)lysine (0.02–0.04 wt %) show phase-matched SHG signals about 10 times larger than quartz near the *b* direction. For a crystals thickness of 1.6 mm, this yields $d_{\mathrm{eff}} = 8 \times 10^{-11}$ esu. This number is in agreement with the $d_{\mathrm{eff}}$ for the nonlinear guest molecules, taking into account the above range of concentrations. Further work is in progress to determine from the SHG measurements the alignment of the various guest molecules in glycine crystals.

**Glutamic Acid·HCl.** Other systems of interest in the present context are noncentrosymmetric crystals which possess directions along which SHG is symmetry forbidden. As an example, we studied mixed crystals of (*S*)-glutamic acid·HCl grown from 5 M HCl solutions. The pure crystals[20],[21] of orthorhombic symmetry $P2_12_12_1$ are nonpolar along the three principal crystallographic axes, and therefore no frequency doubling is expected in these directions, as confirmed by the experiments.[22] We anticipated that (*S*)-glutamic acid·HCl crystallized in the presence of (*S*)-$\alpha$-amino acids with a *p*-nitroaniline moiety in the side chain should yield crystals of lower symmetry than the pure host, with the occluded guest molecules arranged in a polar manner with respect to the crystal axes. Such mixed crystal should give SHG along these axes.

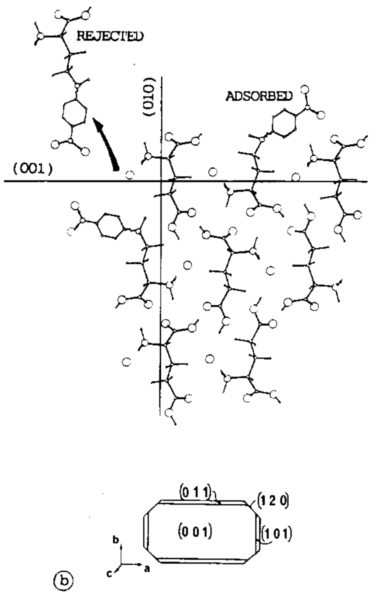

**Figure 4.** (a) Packing arrangement of the (*S*)-glutamic acid·HCl crystal viewed along the *a* axis. (b) Schematic morphology of the crystals.

**Table I. SHG Data for (*S*)-Glutamic Acid•HCl Crystals Grown in the Presence of Several Additives**[a]

| additive | $\bar{k}$ | $\bar{e}_2\bar{e}_1\bar{e}_1$ | $I_2/I_2$ (quartz) |
|---|---|---|---|
| 1 | *b* | *a a c* | 3.1 |
| | *a* | *b c c* | 0.01 |
| | *c* | *a b b* | 0.18 |
| 2 | *b* | *a a c* | 0.47 |
| | *a* | *b c c* | 0.0041 |
| | *c* | *a b b* | 0.19 |
| 3 | *b* | *a a c* | 2.6 |
| | *a* | *b c c* | 1.6 |
| | *c* | *a b b* | 0.0061 |
| 4 | *b* | *a c c* | 0.77 |
| | *a* | *b c c* | 0.37 |
| | *c* | *a b b* | 0.085 |
| 5 | *b* | *a a c* | 10.0 |
| | *a* | *b c c* | 0.71 |
| | *c* | *a b b* | 0.020 |
| 6 | *b* | *a a c* | 28.0 |
| | *a* | *b c c* | 0.021 |
| | *c* | *b b b* | 0.0041 |

[a] $\bar{k}$ denotes the wave vector of the fundamental beam; $\bar{e}_1$ and $\bar{e}_2$ are unit vectors along the fundamental and harmonic electric fields; *a*, *b*, and *c* denote the crystallographic axes; $I_2$ represents the second harmonic intensity.

The packing arrangement and the morphology of (*S*)-glutamic acid·HCl crystals are depicted in Figure 4. When the platelike crystals are grown unidirectionally along the *c* axis, the guest molecules of the same absolute configuration may occupy only two out of four different 001 surface sites and upon occlusion should reduce the symmetry to $P112_1$. The results of SHG measurements along

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[19] Weissbuch, I.; Addadi, L.; Lahav, M.; Leiserowitz, L. *J. Am. Chem. Soc.* **1988**, *110*, 561.

[20] Sequeira, A.; Rajagopol, H.; Chidambaram, R. *Acta Crystallogr., Sect. B* **1972**, *28*, 2514.

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[22] Pure crystals of (*S*)-glutamic acid·HCl generate second harmonic signals about $3 \times 10^3$ stronger than quartz in a direction 50° off the *c* axis in the *bc* plane.

the three crystallographic axes, for (*S*)-glutamic acid·HCl crystals containing various additives, are summarized in Table I.[23] All mixed crystals show SHG along each of the three crystallographic axes, indicating a loss of the 2-fold screw symmetry along these axes. However, the SHG intensity depends strongly on the particular crystallographic axis chosen as the propagation direction. All mixed crystals show the strongest SHG along the *b* axis in a type II interaction; i.e., a maximum SHG signal is obtained for a fundamental field making an angle of 45° with the *a* and *c* axes, giving rise to a second harmonic field polarized along the *a* axis. For propagation direction along the other two axes (*a* and *c*), the interaction is of type I with the SHG field polarized normal to the fundamental field as shown in the table. Unlike the glycine mixed crystals, there are dramatic differences in the SHG intensity between crystals containing guest molecules possessing odd and even numbers of methylene groups in their side chains, indicative of the alignment of the highly hyperpolarizable end group. For crystals containing $N^{\epsilon}$-(*p*-nitrophenyl)lysine, $N^{\epsilon}$-(2,4-dinitrophenyl)lysine, and $N^{\delta}$-(2,4-dinitrophenyl)ornithine, the distinct SHG signal along the *c* axis leaves no doubt as to a loss of the 2-fold screw symmetry along this axis resulting in triclinic $P1$ symmetry. For the (*S*)-glutamic acid·HCl crystals containing $\gamma$-glutamyl-(*p*-nitrophenyl)hydrazide and $N^{\gamma}$-(*p*-nitrophenyl)-$\alpha$,$\gamma$-diaminobutyric acid the extremely weak SHG signals along the *c* axis suggest a tendency toward retaining a 2-fold screw symmetry about the *c* axis. However, from the present data it is difficult to determine the relative occupancies of the guest molecule's sites related by 2-fold screw symmetry along *c*. The system (*S*)-glutamic acid·HCl with $N^{\delta}$-(*p*-nitrophenyl)ornithine, which also has a relatively weak SHG efficiency along *c*, is a special example insofar as it is possible that the hyperpolarizable *p*-nitroaniline group, exhibiting pseudo 2-fold symmetry in terms of molecular dipole moment, is probably aligned almost parallel to the *c* axis.

It should be noted that these host/guest systems of glycine and of (*S*)-glutamic acid-HCl, which show undeniable $P1$ symmetry, also provide information as to the texture of the growing layer face of the crystal: (010) for glycine and (001) for glutamic acid·HCl. We may envisage, certainly in the case of glutamic acid·HCl where the 002 layer is ~6.6 Å thick, that the side chain of the adsorbed additive molecule will tend to point away from the moving ledge of the growing 002 layer, thereby reducing the local site symmetry about the ledge and consequently the symmetry of the layer. If the layer growth is nucleated such that the growing ledges move in the same direction layer after layer, we may envisage that the crystal will be composed of sectors within each of which the side chains of the guest molecules will preferentially point in the same direction, leading to a $P1$ symmetry. This additional reduction in symmetry from the idealized one could not be extracted from the various techniques already applied, e.g., morphological and etch figure symmetries.[24]

In conclusion, we have demonstrated by SHG measurements that guest molecules can be adsorbed and preferentially occluded through different subsets of surface sites on crystallographically different faces, leading to a mixed crystal of sectors of reduced symmetry. In this way, it is possible to induce guest molecules to be aligned in a polar arrangement in a nonpolar crystal, making the latter susceptible to all second-order optical nonlinear effects. Several examples of mixed crystals have been discussed for which the appearance of a SHG signal undeniably shows a loss of the crystallographic center of inversion. This work has demonstrated the potential of SHG to become a novel useful analytical tool to study the orientation of minor amounts of additive occluded in a solid matrix. It is furthermore believed that this approach opens the way to molecular engineering of more efficient optical nonlinear materials to be used for wavelength conversion. Further work is in progress to determine the second-order susceptibility tensor elements in these mixed crystals as a function of the orientation of the occluded guest molecules.

**Acknowledgment.** We thank E. Wasserman for his hospitality and him and L. Addadi for stimulating discussions. We are grateful to E. Shavit and J. Kelly for their skillful help. We acknowledge financial support from the Israel Academy of science and Humanities and the Minerva foundation.

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(23) The relative second harmonic intensities shown in the table can vary by 1 order of magnitude or more as the sample is translated through the beam. These variations are attributed to (1) a varying optical path length inside the sample, inducing a large variation in SHG intensity through a shift in the Maker fringes, (2) the relatively poor optical quality of the samples, and (3) the anisotropic distribution of the occluded additive molecules in the bulk of the mixed crystals. When comparing the doubling efficiency of the various mixed crystals, one should keep in mind the SHG dependence on both the concentration of the additive and the coherence length of the material, which are generally different in each compound.

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