A New Organic Material Exhibiting Highly Efficient Phase-matched Second Harmonic Generation: 4-Methoxy-4′-nitrotolan

Takashi Kurihara, Hisao Tabei, and Toshikuni Kaino

NTT Electrical Communications Laboratories, Tokai, Ibaraki-ken, 319-11, Japan

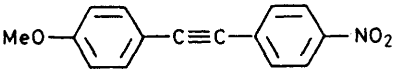
The high second harmonic efficiency with phase-matchable characteristics of a new nonlinear optical material, 4-methoxy-4′-nitrotolan, is reported.

Non-centrosymmetric crystals of organic molecules, in particular of donor–acceptor substituted π-conjugated compounds having large electric dipole moments and transition moments, may show high efficiency for second harmonic generation (S.H.G.). The most common organic molecules reported for second-order nonlinear optical materials are benzene derivatives, substituted by amino and nitro groups, one of the strongest donor–acceptor pairs of substituents.[1] Typical examples are 2-methyl-4-nitroaniline (MNA) and *N*-(4-nitrophenyl)-L-prolinol (NPP). In these compounds, nonlinear optical properties at the molecular level are reflected well at the crystalline level by non-centrosymmetric crystal structures.[2,3] In order to obtain new materials with greater S.H.G. efficiency than MNA or NPP π-conjugated aromatic systems with larger transition moments than that of the benzene ring are required. We now describe a new second-order nonlinear optical material, 4-methoxy-4′-nitrotolan (MNT), exhibiting highly efficient phase-matched S.H.G. Tolan was selected as a π-conjugated system because it has transition moments twice as large as that of the benzene ring.

In MNT, methoxy- and nitro-substituents are the donor and acceptor respectively, at the tolan 4,4′-positions. MNT was prepared in good yield by cross-coupling between 4-ethynylanisole and 4-iodonitrobenzene using Takahashi's method.[4] Fine crystals of MNT were precipitated from a methylcyclohexane solution by slow cooling. Several yellow needles of dimensions *ca.* $1 \times 1 \times 20$ mm^3 were obtained. S.H.G. efficiency was measured by the Kurtz powder method.[5] Studies were performed on powders with grain sizes in the following ranges <25, 25—40, 40—63, 63—88, and 105—120 μm. A Nd : YAG laser (λ 1.06 μm; 8 kW/cm^2) was used as the optical source and directed onto the powdered samples through a u.v.–visible cut-off filter. The 0.53 μm radiation was collected by a monochromator after separating the 1.06 μm pump beam with an i.r. cut-off filter. S.H.G. intensities were detected by a photomultiplier tube. The S.H.G. intensity of the 105—120 μm grain size MNA powder was used as the standard.

From the relationship between S.H.G. intensity and particle size, it is possible to decide if a crystalline powder is phase-matchable or nonphase-matchable.[5] For the former, S.H.G. intensity increases linearly with increasing particle size and saturates at a certain value. For the latter, S.H.G. intensity attains its maximum value when the particle size is close to the coherence length, usually 20—30 μm, and decreases as the particle size increases.

The relation between S.H.G. intensity and particle size for MNT and MNA powders is shown in Figure 1. The S.H.G. intensity of MNA decreased with increasing particle size after attaining a maximum at the coherence length. Thus, MNA is nonphase-matchable for S.H.G. This result agrees with the fact that the d_{11} tensor, which is the maximum hyperpolarizability, of a single MNA crystal could not produce birefringence phase-matching.[6] In contrast, the S.H.G. intensity of MNT continues to increase beyond the coherence length and attains a value twice that for 105—120 μm grain size MNA. This behaviour suggests that MNT crystalline powders are phase-matchable for S.H.G. Since phase-matched S.H.G. is more efficient at larger crystal sizes, MNT is thought to be a practical organic crystal for use in optically nonlinear devices such as frequency mixers and parametric oscillators.



MNT

The fact that MNT is 'active' in S.H.G. obviously suggests that there is some mechanism preventing a centrosymmetric crystal structure. Two possible mechanisms connected with molecular structure features may be considered. One is the depression of the molecular dipole moment in the ground state, and the other is the existence of a strong driving force that overcomes the intermolecular dipole–dipole electrostatic interaction.

Concerning the depression of the molecular dipole moment, the methoxy group of MNT can be considered to be a moderate electron donor when its Hammett substituent constant σ is compared with that of the amino group.[1] This choice of a moderate electron donor in MNT prevents molecular dipoles from locating in opposite directions by intermolecular dipole–dipole electrostatic interaction.

Concerning the driving force in the crystallization process, the π-conjugated tolan system is considered to induce a van der Waals interaction strong enough to be comparable to the intermolecular dipole–dipole electrostatic interaction, which causes centrosymmetry. In many efficient second-order nonlinear optical materials, noncentrosymmetric crystal structures were attained owing to the presence of intermolecular

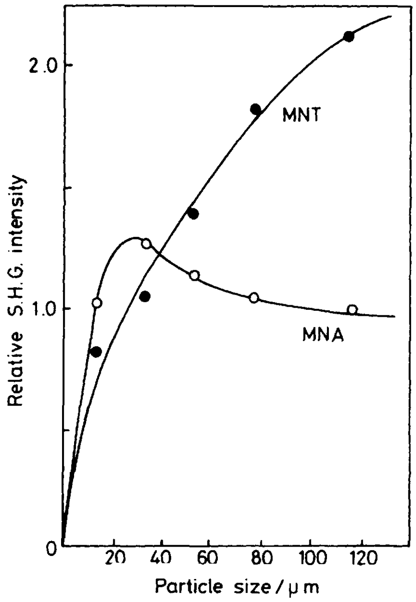


Figure 1. Particle-size dependence of S.H.G. intensity for MNT and MNA powders.

hydrogen bonding. It is assumed that the contribution of van der Waals interaction in MNT is analogous to that of intermolecular hydrogen bonding in NPP or urea.[3,7]

In conclusion, it is clear that tolan serves as an excellent π-conjugated system for constructing highly efficient second-order nonlinear materials. By appropriate combinations of donor–acceptor pairs and additional substituents which control intermolecular interactions, optical nonlinear materials with high efficiencies may be obtained.

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