Chem. Mater. 1991, 3, 3-4

Communications

Second-Order Nonlinearities and Crystal Structure of 2-Methoxy-4′-nitro-(*E*)-stilbene

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Received April 17, 1990
Revised Manuscript Received November 6, 1990

Second-order nonlinear optical (NLO) properties of crystalline materials depend both on the magnitude of the molecular hyperpolarizability (β) and on the orientation of the chromophores in the crystal lattice.[1] If the molecular hyperpolarizability is to result in a nonzero macroscopic nonlinearity, the molecule must crystallize in a noncentrosymmetric space group. The design of new second-order NLO materials requires one both to address the structure–property relationships that govern β and to develop methodologies that favor noncentrosymmetric crystallization. Methods used to encourage noncentrosymmetric crystallization include the use of chiral molecules,[2] the incorporation of functional groups that encourage asymmetric intermolecular hydrogen bonding,[3] the synthesis of molecules with very small ground-state dipole moments but larger excited-state dipole moments,[4] and the variation of counterion with ionic chromophores.[5,6]

To develop molecular structure–property relationships, it is important to measure accurate values of β for many series of compounds. These values, which can be obtained by electric-field-induced second harmonic generation (EFISH) experiments, coupled with theoretical modeling will provide guidelines for the synthesis of new NLO materials. Recently Cheng et al. have examined the effect that variation of donor and acceptor strength has on β, for various aromatic systems, including benzenes and stilbenes.[7] In collaboration with Cheng, we are now studying the effect on the magnitude of β of variation of the relative substitution position of the donor and acceptor in stilbenes.

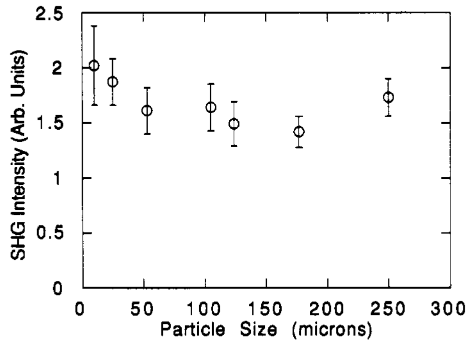

Figure 1. Plot of SHG intensity (arbitrary units) as a function of particle size (micrometers) for compound **2**. Each point actually corresponds to a range of particle sizes roughly centered on the value indicated.

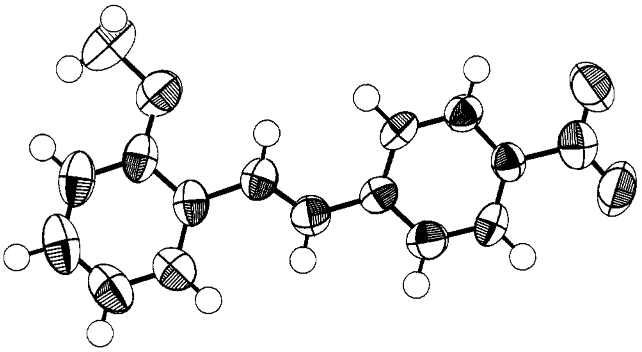

Figure 2. ORTEP drawing of **2** with 50% thermal ellipsoids. Hydrogen atoms are given arbitrary, small thermal parameters.

We chose to examine the x-methoxy-y'-nitrostilbenes (where x and $y' = 2, 3, 4$) in detail because of the large β of 4-methoxy-4′-nitro-(*E*)-stilbene, **1**, which can serve as a reference, and the availability of the nine isomers.[8]

While routinely screening organic materials synthesized in our laboratory for second harmonic generation powder efficiency by a modification of the Kurtz powder technique,[9] we found that 2-methoxy-4′-nitro-(*E*)-stilbene, **2**,[10] has a second harmonic generation (SHG) powder efficiency ~150–350 times that of a urea reference. We used the 1064-nm output of a Q-switched Nd:YAG laser in a dual-beam system (using a urea sample in the reference arm) to provide normalization of the SH signals for laser shot-to-shot fluctuations. Pulse energies used were in the range 100–500 μJ with spot sizes of 2–3 mm. The diffusely backscattered SH signals were collected and isolated by using filters and a monochromator. The SH signals were detected by using photomultiplier tubes (Hamamatsu R406) whose outputs were amplified and integrated by using 10-ns gate widths. Lightly ground unsized micro-

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[†] Contribution 8127.

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(10) Characterizing data for **2**: ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.23 (d, J = 7.0 Hz, 2 H, CHCN), 7.83 (d, J = 6.9 Hz, 2 H, C*H*CHCN), 7.74 (d, J = 16.7 Hz, 1 H, CH=C*H*CCO), 7.71 (dd, J = 7.6, 1.5 Hz, 1 H, OC$_1$CHCHCHC*H*), 7.39 (d, J = 16.6 Hz, 1 H, C*H*=CHCCO), 7.33 (td, J = 7.4, 1.3 Hz, 1 H, OCCHCHC*H*CH), 7.06 (d, J = 7.9, Hz, 1 H, OCC*H*CHCHCH), 6.99 (d, J = 7.4, Hz, 1 H, OCCHC*H*CHCH), 3.90 (s, 3 H, CH$_3$). Anal. Calcd for C$_{15}$H$_{13}$NO$_3$: C, 70.58; H, 5.13; N, 4.39. Found: C, 70.74; H, 5.27; N, 5.45.

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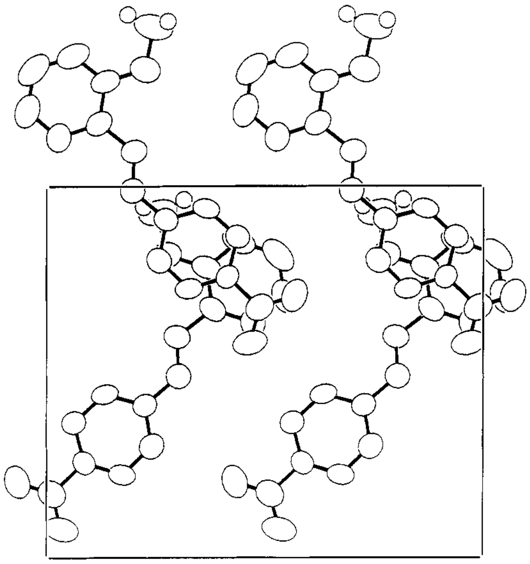

Figure 3. ORTEP drawing of **2** showing the packing of molecules in the unit cell (outlined). The view is down the *b* axis; hydrogen atoms are omitted for clarity.

crystalline powders of **2** ranged from about 40 to 150 μm. Given the possibility of preferential orientation of particles in assembling the samples, the uncertainties in the measured efficiencies can be quite large, perhaps a factor of 2 or more. A plot of SHG intensity as a function of particle size will reach a maximum and level off for a phase-matchable material; in contrast, if a material is not phase matchable, the SHG intensity will reach a peak value and then decrease to a small value. We have examined the particle-size-dependent SHG intensity for **2**, and the data are consistent with **2** being a phase-matchable material (Figure 1).

The UV-visible spectrum of **2** has a band centered at 368 nm (ϵ = 22 500 M^{-1} cm^{-1}) in acetone. The cutoff (50% transmission) for a saturated solution of **2**, in acetone, is at 490 nm and for a 210 ± 30 μm thick single crystal it is at 465 nm. The transparency and the powder SHG efficiency exhibited by **2** make it worthy of further study as a potential material for second harmonic generation. The crystal structure of **2** was determined to find the orientation of the molecule in the lattice. The compound crystallizes in the orthorhombic, noncentrosymmetric space group $Pna2_1$.[11] Distances and angles are generally as expected. An ORTEP drawing of **2** is shown in Figure 2. The molecules stack in the cell parallel to the *ac* plane, with π–π interactions as short as 3.45 (C6–C13) and 3.45 Å (C3–O3). Most other interplane interactions are in the range 3.55–3.8 Å (Figures 3 and 4). The planes of the molecules themselves are all nearly parallel, but their axes meet at angles of about 100°. The herringbone pattern is in part responsible for the large powder SHG efficiency of **2**. In the space group $Pna2_1$ the optimal angle between the symmetry-related donor–acceptor vectors of the chromophores for phase-matched SHG is 109.4°. Thus crystals of **2** may undergo efficient phase-matched SHG.[12]

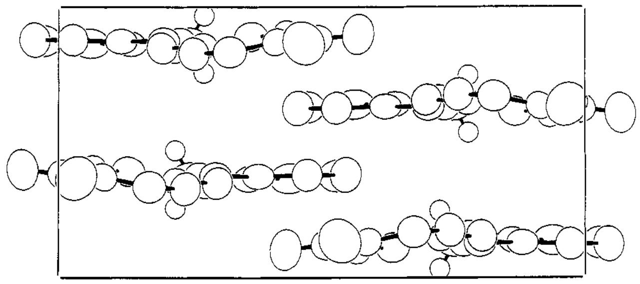

Figure 4. Packing drawing, showing the unit cell of **2** and four molecules. Hydrogen atoms are included only on the methyl carbon atom of the methoxy groups.

To our knowledge only one compound in the literature has a powder SHG efficiency larger than that of a compound **2** (SH at 532 nm), a related compound, 3-methyl-4-methoxy-4′-nitro-(*E*)-stilbene, **3**, which has been reported to have a nonlinearity roughly 750–1250 times that of urea.[13] Both compounds contain two molecular features that may contribute to the large observed macroscopic nonlinearity. These are a relatively weak donor[13] (compared to dialkylamino) or acceptor, and molecular asymmetry. Both features may favor the noncentrosymmetric orientation of the chromophore in the lattice, as discussed below. Since dipole–dipole interactions tend to favor antiparallel packing, it may be desirable to minimize the ground-state dipole when working with neutral molecules.[13] Both **2** and **3** have a relatively weak donor group (methoxy) which results in a relatively small ground-state dipole moment (4.8 for **2** as compared to 6.2 for 4-dimethylamino-4′-nitro-stilbene[8]). In addition, both compounds have groups (the methoxy group for **2** and the methyl group for **3**) that lower the symmetry of the molecule; this also tends to increase the probability of achieving noncentrosymmetric crystallization.[3] It is worth noting that both compounds have similar crystal motifs, dominated by π–π stacking with the donor of one ring sitting over the acceptor of the other ring, and a roughly 90–100° angle between the molecular axes.

In summary, we have found that the yellow compound, 2-methoxy-4′-nitro-(*E*)-stilbene, possesses a large powder second harmonic generation efficiency. This observation, the particle-size-dependent SHG study, and the crystal structure suggest that this compound may be of interest for second harmonic generation in the visible region.

Acknowledgment. The research described in this paper was performed, in part, by the Jet Propulsion Laboratory, California Institute of Technology, as part of its Center for Space Microelectronics Technology, which is supported in part by the Strategic Defense Initiative Organization, Innovative Science and Technology Office through an agreement with the National Aeronautics and Space Administration. The diffractometer used in this study was purchased with a grant from the National Science Foundation, CHE-8219039. We thank Bruce G. Tiemann, Paul Groves and Kelly Perry for technical assistance.

Registry No. 2, 28915-66-4.

Supplementary Material Available: ORTEP drawing of the molecule 2-methoxy-4′-nitro-(*E*)-stilbene with atom numbering, details of the data collection and refinement, tables of crystal data, final parameters of all the atoms, and complete distances and angles (11 pages); observed and calculated structures factors (6 pages). Ordering information is given on any current masthead page.

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(11) $C_{15}H_{13}NO_3$: mol wt 255.28, orthorhombic $Pna2_1$ (No. 33), a = 14.422 (6) Å, b = 7.329 (2) Å, c = 12.237 (7) Å, V = 1293.4 (10) Å^3, Z = 4. Mo Kα radiation, 3941 reflections collected, 1196 independent used in refinement, full-matrix least-squares, R for 848 reflections ($R = \sum|F_o - |F_c|| / \sum F_o$, where F_o and F_c are the observed and the calculated structure factors) with $F_o^2 > 0$ = 0.046, goodness of fit $([\sum w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$, where w = the weight of the reflection, n = the number of data, and p = the number of parameters refined) = 2.06. All non-hydrogens were refined anisotropically. Hydrogen atom parameters were assigned from difference maps or by calculation with C–H = 0.95 Å.

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