CHEMISTRY ===

First Organophosphorus Nonlinear-Optical Media

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Molecular crystals occupy a place among nonlinearoptical materials owing to their high nonlinear susceptibilities [1–4]. This feature depends directly on the degree of charge transfer in the molecules that form the crystal [1]. Systems with intramolecular charge transfer are usually heteroatomic and functional organic compounds with extended electron conjugation [2]. By varying the nature of the heteroatom or the function incorporating the heteroatom, it is possible to vary the degree of charge transfer and, thus, to perform controlled synthesis of new highly efficient nonlinear-optical materials [2–4]. To the best of our knowledge, no data on the use of organophosphorus compounds as nonlinear-optical media have been published.

Using the powder method [5], we found for the first time that the crystals of the *E,E,E* and *Z,Z,Z* isomers of tristyrylphosphine oxide (1a, 2a) and tristyrylphosphine sulfide (1b, 2b) generate the second harmonics of the radiation from a neodymium laser with an efficiency comparable to that for a classical nonlinear-optical material, lithium iodate. The intramolecular charge transfer in compounds 1 and 2 is made possible by the conjugation of the π -electron-donating benzene rings with the electron-withdrawing phosphoryl (or thiophosphoryl) group through the double bonds of the styryl fragments.



X = O(a), S(b)

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The *Z*,*Z*,*Z* isomers **2a** and **2b** were synthesized under mild temperature conditions $(20-100^{\circ}\text{C})$ by a known method [6] involving oxidation (or sulfonylation) of *Z*,*Z*,*Z*-tristyrylphosphine (**3**), readily available through the direct reaction between elemental phosphorus and phenylacetylene [7, 8]. The *E*,*E*,*E* isomers **1a** and **1b** were prepared by heating (100–150°C) of phosphine **3** in DMSO or in an elemental sulfur–toluene system, respectively.

Thus, the discovery of nonlinear-optical properties in compounds 1 and 2 is a real prerequisite for controlled synthesis of their structural analogues with a specified degree of intramolecular charge transfer, i.e., new classes of organophosphorus nonlinear-optical materials with controlled characteristics.

E,E,E-Tristyrylphosphine oxide (1a). Phosphine 3 was heated (100°C, 50 h) in DMSO, and the solvent was evaporated in a vacuum to give phosphine oxide 1a (80%) as colorless crystals, mp 246–248°C (DMSO). The spectroscopic characteristics (IR, ¹H NMR, ³¹P NMR) of phosphine oxide 1a were identical to those for an authentic sample [9].

E,E,E-Tristyrylphosphine sulfide (1b). Phosphine 3 was heated (145–150°C, 12 h) with an equimolar amount of elemental sulfur in xylene, the solvent was distilled off, and the residue was recrystallized from hexane to give phosphine sulfide 1b (40%) as light yellow crystals, mp 226–228°C (DMSO). ¹H NMR (CDCl₃, δ , ppm): 6.68 (dd, 3H, H–C-1, ³*J*_{HH} = 16.8 Hz, ²*J*_{PH} = 21.5 Hz), 7.35–7.37 (m, 9H, *p,m*-Ph), 7.51–7.52 (m, 6H, *o*-Ph), 7.53 (dd, 3H, H–C-2, ³*J*_{PH} = 22.9 Hz). IR (KBr, cm⁻¹): 3061, 3022, 2983 (v, C–H); 1610, 1573, 1494, 1447 (v, C=C, Ph); 1320, 1290, 1232, 1191, 1174 (δ , C–H); 997, 977, 880 (δ , HC=CH); 845, 834 (v, P=S); 798 (v, P–C); 743, 689 (δ , C–H arom); 610 (δ , C–P–C).

For C₂₄H₂₁PS anal. calcd. (%): C, 77.42; H, 5.65; P, 8.33; S, 8.60.

Found (%): C, 77.80; H, 5.36; P, 8.74; S, 8.50.

Z,*Z*,*Z*-**Tristyrylphosphine oxide (2a) and sulfide (2b)** were prepared by treating *Z*,*Z*,*Z*-tristyrylphosphine with aqueous hydrogen peroxide or elemental sulfur according to a known procedure [6].

The generation of the second harmonics was studied by the powder method using the radiation from a FIRST ORGANOPHOSPHORUS NONLINEAR-OPTICAL MEDIA

neodymium laser on an yttrium aluminum garnet (with a wavelength of 1064 nm) operating in the Q-modulation mode. The pulse power density for the exciting radiation was $\sim 10^8$ W/cm². The spectrum of the arising emission of the samples contained a line at 532 nm with a width of ~1 nm, corresponding to the error of measurement for the spectrometer used.

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