Synthesis of Diarylthiobarbituric Acid Chromophores with Enhanced Second-Order Optical Nonlinearities and Thermal Stability

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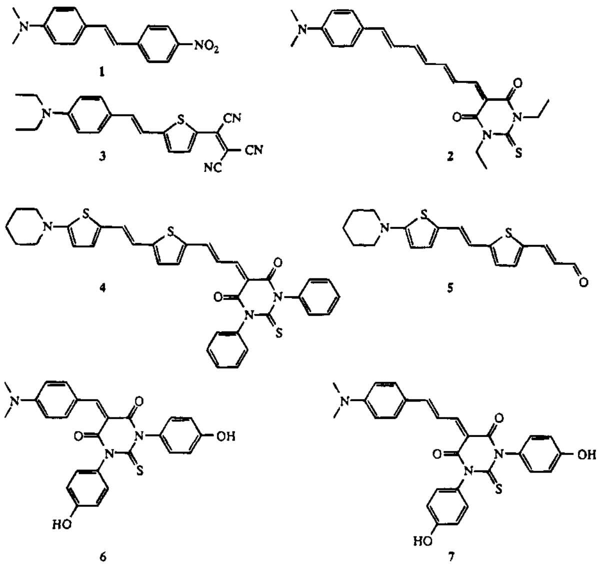
There is substantial effort being devoted to developing poled organic polymers for electrooptic applications.[1] If this technology is to compete with inorganic crystalline materials, it is necessary to (i) incorporate a high density of chromophores with large optical nonlinearities into a polymer, (ii) achieve a high degree of alignment of these chromophores, and (iii) lock in this alignment for long periods (years) even at elevated temperatures (at least 80 °C).[2] In poled polymer systems, the alignment is locked in place either by using host polymers with high glass transition temperatures,[3] at least 125−150 °C above the anticipated operating temperature, or by cross-linking the chromophore polymer−composite.[4] In either case, it is necessary to develop highly nonlinear chromophores that are thermally robust at temperatures in excess of 200 °C and, preferably, that are covalently attachable to polymers. Recently, theoretical[5] and experimental[6] studies suggest that chromophores with strongly aromatic ground states such as 4-(*N*,*N*-dimethylamino)-4′-nitrostilbene, **1** (Scheme 1) will tend to have only moderate nonlinearities. Thus, for **1**, the dot product of the dipole moment and the first hyperpolarizability, $\mu\beta$, which is the relevant parameter for poled polymer applications, is 480×10^{-48} esu.[7] It has been shown that by reducing the ground-state aromaticity by either replacing the phenyl groups with heterocyclic rings that lose less aromatic stabilization energy upon charge separation,[6a−c] or by using extended conjugated π-systems that incorporate acceptors such as 3-phenyl-5-isoxazolone[6d] and diethylthiobarbituric acid,[6a] very large nonlinearities can be achieved. In the case of the diethylthiobarbituric acid chromophores such as **2** (Scheme 1) for which $\mu\beta = 9800 \times 10^{-48}$ esu,[6d] the polyene chain of this chromophore does not have the requisite thermal stability to be poled at temperatures in excess of 200 °C.[8] In contrast, many of the heterocyclic chromophores, including **3** (Scheme 1) exhibit excellent thermal stability well in excess of 200 °C.[3b] In addition, Moylan et al.[9] and we[10] have found that replacement of the ethyl groups in diethylthiobarbituric acids with aryl groups leads to chromophores with excellent thermal stability. Motivated to develop thermally robust and highly nonlinear chromophores, and building upon the observations described above, we set out to synthesize chromophore **4** (Scheme 1). It was our hope that replacement of (i) the phenyl groups and extended polyene fragment in **2**, with the thiophene−vinyl−thiophene bridge in **4**, and (ii) the ethyl groups on the thiobarbituric acid with phenyl groups would significantly improve the thermal stability without sacrificing the nonlinearity. To minimize steric interactions between the diphenylthiobarbituric acid and thiophene rings that could preclude their coplanarity, a vinyl group was incorporated between the thiophene bridge and the diphenylthiobarbituric acid ring. Com-

Scheme 1



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pound **4** was prepared by reaction of **5**[11] (Scheme 1) with diphenylthiobarbituric acid in acetic anhydride. Chromatography of the crude **4** material on silica gel eluting with dichloromethane and hexane (1:1) gave a blue solid on evaporation to dryness. After recrystallization from dichloromethane compound **4** was isolated in 24% yield and was characterized by ^{1}H nuclear magnetic resonance (NMR), ultraviolet–visible, and mass spectroscopies.[12] Electric-field-induced second harmonic generation[7] experiments on **4**, performed at two different laboratories, at 1.907 μm in chloroform (DuPont) and in dichloromethane (EniChem America), were in good agreement, both giving $\mu\beta$ products of 8600×10^{-48} esu. In both of these solvents, the absorption maximum for **4** was at 710 nm and thus the correcting these values for dispersive enhancement using the two-level correction,[13] gave zero a frequency value, $\mu\beta(0)$, of 3300×10^{-48} esu, which is approaching an order of magnitude greater that for **1** ($\mu\beta(0)$ of 370×10^{-48} esu). Thermal stability studies on **4** dissolved in poly(methyl methacrylate), PMMA, in which the absorption spectra were monitored before and after heating a sample at temperatures up to 210 °C for 30 min, showed less than 10% change (at the absorption maximum). Furthermore, when **4** was poled as a host–guest system in PMMA at 0.5 mol % and 1 MV cm^{-1} poling field, the resulting polymer had an electrooptic coefficient, r_{33}, of 2.6 pm V^{-1} measured at 1.3 μm, consistent with the large molecular nonlinearity. Chromophore solubility prohibited incorporating concentrations greater than 1 mol % of this chromophore in PMMA. Since covalent attachment of chromophores to polymers via one or more bonds, in general, allows for incorporation of higher concentrations of chromophores and leads to improved temporal stability, we decided to synthesize a functionalized diarylthiobarbituric acid. Thus, reaction of bis(4-acetoxyphenyl)thiourea[14a] with malonic acid and acetyl chloride gave, after deprotection of the hydroxy group in aqueous base, and acidic workup, crude bis(4-hydroxyphenyl)thiobarbituric acid.[14b] This crude material reacted cleanly with 4-(*N,N*-dimethylamino)benzaldehyde or 4-(*N,N*-dimethylamino)cinnimaldehyde in tetrahydrofuran, THF, to give **6**[12] and **7**[12] (Scheme 1), respectively, as microcrystalline precipitates, which after filtration were isolated in analytically pure form. These compounds demonstrate that functionalized diarylthiobarbituric acid chromophores suitable for covalent attachment to polymers can be synthesized.

In summary, the compounds reported here demonstrate that it is possible to design chromophores that simultaneously exhibit large nonlinearity and good thermal stability. Furthermore, with the synthesis of bis(4-hydroxyphenyl)thiobarbituric acid, we believe that it should be possible to covalently incorporate these and other rather nonlinear chromophores into poled polymers at high concentrations. Experiments to test this hypothesis are in progress.

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Supplementary Material Available: Synthesis procedures, ^{1}H NMR, mass spectral, and analytical data for **4**, **6**, and **7** (3 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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