Ketene Dithioacetal as a π-Electron Donor in Second-order Nonlinear Optical Chromophores

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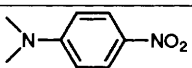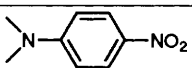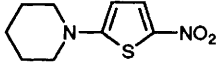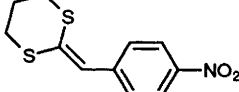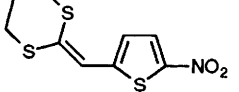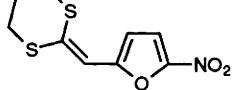
It is shown experimentally that the ketene dithioacetal group is very effective as an electron-donating group in the design and synthesis of thermally stable and efficient second-order nonlinear optical chromophores.

In the design of highly efficient second-order nonlinear optical (NLO) chromophores for electrooptic device applications, asymmetric conjugated molecules containing donor and acceptor substituents have been thoroughly scrutinized.[1] Molecular nonlinearity ($\beta\mu$) of such compounds is dependent on the effective length of π-conjugation and the strength of donor and acceptor substituents.[2-15] while a variety of acceptors such as carbonyl, n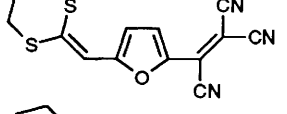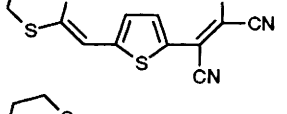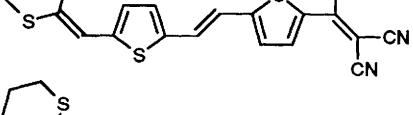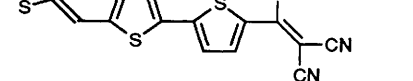itro, sulfonyl,[5] disulfonylvinyl,[6] dicyanovinyl,[7] cyanonitrovinyl,[8] tricyanovinyl,[9] thiobarbituric acid[10] and rhodanine[11] have been examined for their role in influencing the molecular NLO properties, a few electron-donors such as alkoxy and dialkylamino groups have received the most attention. Lehn and coworkers,[12] in their recent studies on push–pull carotenoids, have discussed the role of
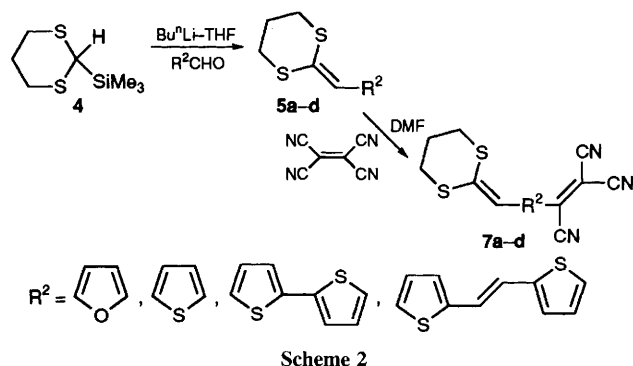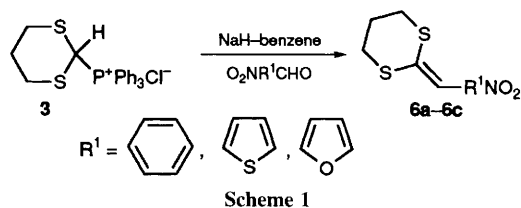
benzodithia group as an electron donor. In this communication, we demonstrate the important role of ketene dithioacetal group as an electron donor in the design and synthesis of efficient and thermally stable NLO chromophores.

Table 1 lists all the donor–acceptor substituted compounds studied in this work. Ketene dithioacetal group is used as an electron donor in all the compounds except for **1** and **2**. The latter compounds, which are studied only for comparative purposes, possess dialkylamino and nitro substituents. While N,N-dimethylamino-4-nitrobenzene **1** was obtained commercially, 2-piperidino-5-nitrothiophene **2** was synthesized by the nucleophilic substitution reaction between piperidine and 2-bromo-5-nitrothiophene. Different synthetic methodologies (Schemes 1 and 2) were adopted to synthesize the nitro

Table 1

Compound		λ_{max}/nm (in dioxane)	$\beta\mu$ (10^{-48} esu) at $\lambda = 1.907\ \mu m^a$
1		370	110 (90)
2		430	125 (102)
6a		380	130 (110)
6b		438	200 (150)
6c		418	180 (138)
7a		542	850 (528)
7b		558	940 (565)
7c		612	3420 (1803)
7d		595	1500 (829)

^{a} Values in parenthesis represent $\beta_0\mu$, zero-frequency hyperpolarizability product, obtained from the extrapolation of the measured $\beta\mu$ values using a two-level model [ref. 13(b)]

Scheme 1

Scheme 2

To further increase the thermal stability, we designed **7d** by eliminating the olefinic linkage between the thiophene rings in **7c**. Studies indicate that the bithiophene **7d** possesses much higher thermal stability (300 °C) and significantly lower molecular nonlinearity (1500 × 10^{-48} esu) than **7c**. The higher thermal stability of these bithiophene derivatives[15] makes them more important in the development of organic electro-optic materials, despite their lower molecular nonlinearity in comparison with the corresponding thiophene-stilbene derivatives.

In conclusion, we have demonstrated the important role of ketene dithioacetal group as an electron donor in the design of efficient and thermally stable NLO chromophores. Considering the availability of synthetic methods[18] to displace the olefinic proton of the ketene dithioacetal group with hydrocarbon chains, this class of compounds can be covalently incorporated into polymer matrices to develop thermally stable cross-linked polymeric materials for electrooptic device applications.

derivatives **6a–c** and tricyanovinyl derivatives **7a–d**. For the nitro compounds, the ketene dithioacetal group[16] was introduced by reacting the nitro substituted conjugated aldehydes with the Wittig ylide generated from 1,3-dithian-2-yltriphenyl phosphonium chloride, **3** (Scheme 1). The tricyanovinyl derivatives **7a–d** were obtained in a two-step process as shown in Scheme 2. The first step involves the synthesis of **5a–d** by lithiation of 2-trimethylsilyl-1,3-dithiane, **4**, with BuLi and subsequent reaction with the corresponding aldehydes. Reaction of **5a–d** with tetracyanoethylene (TCNE) resulted in tricyanovinyl derivatives **7a–d**, respectively.[17]

Molecular second-order nonlinear optical properties were obtained in nonpolar 1,4-dioxane solvent by the electric-field-induced second harmonic generation (EFISH) technique.[13] The quantity $\beta\mu$, a product of first-order hyperpolarizability and ground-state dipole moment, obtained from EFISH measurements is used to compare the relative efficiencies of the donor–acceptor compounds studied here. Measurements were done at a fundamental wavelength of 1.907 μm primarily to minimize the resonance enhancement complications. For comparison purposes, the zero frequency extrapolated values $(\beta_0\mu)$[13b] are also listed in Table 1.

It is clear from the $\beta\mu$ values obtained for compounds **1** (110 × 10^{-48} esu) and **6a** (130 × 10^{-48} esu) that the ketene dithioacetal group is more effective than the dialkylamino group in increasing the molecular nonlinearity of push–pull compounds. Comparison of $\beta\mu$ values of the corresponding thiophene derivatives **2** (125 × 10^{-48} esu) and **6b** (200 × 10^{-48} esu) reveals the same trend. The data obtained for compounds **6a–c** indicate that heteroaromatic conjugating bridges are superior to benzenoid rings in enhancing the molecular nonlinearity. This observation is in clear agreement with our earlier reported data on donor–acceptor substituted thiophene-stilbenes.[14] This data also suggests that the nature of heteroatom (thiophene being more effective than furan) plays an important role in influencing the molecular NLO properties. With thiophene or furan as conjugating units, enhanced nonlinearities can be achieved by replacing the nitro group with a stronger electron-accepting tricyanovinyl group ($\beta\mu$ = 850 × 10^{-48} esu for **7a**, 940 × 10^{-48} esu for **7b**).

By employing thiophene-stilbene as the conjugating bridge between the donor ketene dithioacetal group and the acceptor tricyanovinyl group, significantly enhanced nonlinearities can be obtained (**7c**, 3420 × 10^{-48} esu). Thermal stability studies indicate that beyond 225 °C, the thiophene-stilbene **7c** undergoes *cis–trans* isomerization followed by decomposition.

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