

Dramatically Enhanced Second-order Nonlinear Optical Susceptibilities in Tricyanovinylthiophene Derivatives

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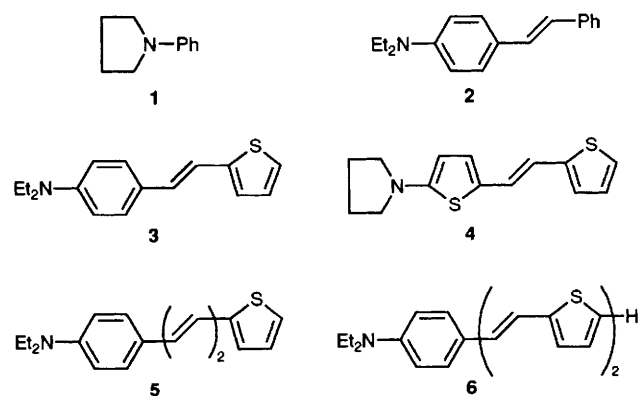
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Experimentally measured second-order nonlinear hyperpolarizability ($\beta\mu$) data for a new series of donor-acceptor conjugated compounds containing tricyanovinyl acceptors and thiophene conjugating units, reveal that this combination results in a dramatic enhancement ($\beta\mu = 6000\text{--}9000 \times 10^{-48}$ esu) of their molecular nonlinearity.

Donor-acceptor substituted organic compounds possessing large molecular second-order nonlinear responses are of current interest because of their applications in electro-optic devices.¹ Numerous classes of donor-acceptor substituted compounds have been explored in recent years to determine the empirical relation between molecular structure and nonlinear response.¹⁻³ The general conclusion is that the molecular nonlinear susceptibility (β) increases with increasing donor and acceptor strengths and with increasing conjugation length. Despite the tidy understanding of these factors, limited success has been achieved in the development of efficient (large β) donor-acceptor compounds due to synthetic and solubility constraints.¹⁻³ We have reported previously two series of donor-acceptor substituted heteroaromatic compounds and demonstrated the importance of the heteroaromatic ring in enhancing their nonlinear responses.⁴ In this communication, we present novel chromophores containing tricyanovinyl acceptors and thiophene conjugating moieties, and show that this combination yields a dramatically enhanced second-order nonlinear hyperpolarizability product ($\beta\mu$).

The use of tricyanovinyl acceptors in nonlinear optical chromophores has been addressed previously by Katz *et al.*⁵ Their studies on *N,N*-dimethylamino-4-tricyanovinylbenzene

($\beta\mu = 850 \times 10^{-48}$ esu, measured at 1.3 μm) and *N,N*-diethylamino-4'-tricyanovinylazobenzene ($\beta\mu = 4095 \times 10^{-48}$ esu, measured at 1.5 μm) reveal that tricyanovinyl acceptors are far superior to dicyanovinyl acceptors (a factor of 2-3) in enhancing the molecular nonlinearity. Despite these remarkable results obtained for tricyanovinyl derivatives, virtually no other donor-acceptor compounds possessing tricyanovinyl

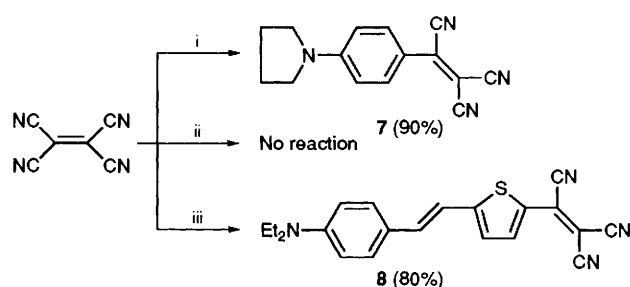


acceptors have been reported to date. Rarity of this class of compounds can be attributed to the difficulty in functionalizing the benzenoid systems (*e.g.* donor substituted stilbenes, Schiff bases and azobenzenes⁹) with the tricyanovinyl group. Our continuing interest in donor-acceptor substituted heteroaromatic compounds for nonlinear optical applications⁴ has prompted us to explore and develop a new series of tricyanovinylthiophene derivatives.

Tricyanovinyl derivatives synthesised and characterised in this work are presented in Scheme 1. 1-Pyrrolidino-4-tricyanovinylbenzene **7** was synthesised by reacting pyrrolidino-benzene **1** with tetracyanoethylene (TCNE) at room temperature.⁷ Attempts to incorporate the tricyanovinyl groups in 4-*N,N*-diethylaminostilbene **2** under various conditions were unsuccessful. However, *N,N*-diethylamino-4-(2-thienylvinyl)-benzene **3** readily reacted with TCNE at room temperature in DMF to give the tricyanovinyl derivative **8** in very high yield.[†] This clearly indicates that electron-rich heteroaromatics such as thiophenes react with tetracyanoethylene more easily than do benzenoid rings. The enhanced reactivity of thiophene derivatives has been used in the synthesis of extended tricyanovinyl derivatives **9**, **10** and **11** from the corresponding dialkylamino-substituted conjugated compounds **4**, **5** and **6** respectively. Precursor compounds **2–6** were synthesised using methodologies developed in our earlier studies.^{4a–c} All the compounds studied here were fully characterised using conventional spectroscopic techniques.

The tricyanovinyl derivatives **7–11** studied here have an intense charge-transfer (CT) band in the visible region of their electronic absorption spectra; they all have a substantially red shifted CT band when compared to the corresponding dicyanovinyl and nitro compounds.^{4a,b} This can be seen clearly from the band maxima data (obtained in dioxane solvent) presented in Table 1 for one set of nitro (**12**), dicyanovinyl (**13**) and tricyanovinyl (**8**) stilbenes. From the absorption data, it may be concluded that the tricyanovinyl acceptor induces much better charge-asymmetry in donor-acceptor compounds.

Second-order hyperpolarizabilities of tricyanovinylated compounds **7–11** were determined using an electric field induced second harmonic generation (EFISH) technique described elsewhere.^{4d} In order to minimize possible resonance enhancement which would exaggerate the measured nonlinear responses, measurements were performed at a



Scheme 1 Reagents and conditions: i, **1** dimethylformamide (DMF), room temp., 24 h; ii, **2**, DMF; iii, **3**, DMF, room temp., 24 h

[†] Data for **8**: ¹H NMR (CDCl₃): δ 7.90 (d, *J* 4.5 Hz, 1H), 7.42 (d, *J* 9 Hz, 2H), 7.26 (d, *J* 15.6 Hz, 1H), 7.13 (d, *J* 4.5 Hz, 1H), 7.00 (d, *J* 15.6 Hz, 1H), 6.67 (d, *J* 9 Hz, 2H), 3.44 (q, *J* 7.2 Hz, 4H) and 1.22 (t, *J* 7.2 Hz, 6H); ¹³C NMR (CDCl₃): δ 161.0, 149.7, 141.8, 139.0, 131.4, 130.2, 127.7, 126.4, 122.2, 114.0, 113.4, 113.1, 113.0, 111.7, 44.6 and 12.6; IR (Nujol): ν 3010, 2940, 2120, 1583, 1514, 1421, 1400, 1259, 1181, 1152 and 1070 cm⁻¹; UV (dioxane): λ 640 and 327 nm; satisfactory elemental analyses were obtained.

fundamental wavelength of 1.907 μm.[‡] And also, for the purpose of comparison, we reduced the β_μ values obtained in this study to the more fundamental quantity β_{0μ}, zero-frequency hyperpolarizability product, using a two-level model.⁸ At this juncture, no attempts were made further to reduce the quantity β_{0μ} to β₀ which requires the evaluation of ground state dipole moment (μ). However, as these molecules are likely candidates to be used as guests or pendant side chains in poled polymer films, the product β_μ is a relevant figure of merit combining both the nonlinearity of the molecule and the ability of the molecule to couple with a macroscopic poling field. The EFISH data obtained for compounds **7–11** are presented in Table 1.

The β_μ value (710 × 10⁻⁴⁸ esu) obtained for 1-pyrrolidino-4-tricyanovinylbenzene **7** is comparable to the value reported in the literature.⁵ Extending the conjugation in **7** by a thienylvinyl moiety results in compound **8** which possesses exceptionally large molecular nonlinearity (β_μ = 6200 × 10⁻⁴⁸ esu). Comparison of the β_μ value of **8** with those of the corresponding nitro and dicyanovinyl stilbenes (**12**, 600 × 10⁻⁴⁸ esu and **13**, 1300 × 10⁻⁴⁸ esu) reveals that the tricyanovinyl acceptor produces a dramatic enhancement of molecular nonlinear response. Furthermore, the β_μ values obtained for compounds **8** and **9** represent the largest values so far reported for stilbene type donor-acceptor compounds. We attribute this observed enhancement of nonlinearity to the lower delocalization energy [28 kcal mol⁻¹ (1 cal = 4.184 J) for thiophene ring *versus* 36 kcal mol⁻¹ for benzene ring] of the

Table 1

Compound	λ _{max} (dioxane)/ nm	β _μ 10 ⁴⁸ esu (λ = 1.907 μm) ^a
7	505	710 (475)
8	640	6200 (3023)
9	718	6900 (2564)
10	662	9100 (4146)
11	653	7400 (3469)
12	478	600 (421)
13	513	1300 (857)

^a Values in parentheses represent β_{0μ}, zero-frequency hyperpolarizability product, obtained from the extrapolation of the measured β_μ values using a two-level model (ref. 8).

[‡] In order to estimate the wavelength dependent resonance enhancement of nonlinearity, compound **8** was measured at both 1.907 μm and 1.54 μm wavelengths. The magnitude of β_μ (15000 × 10⁻⁴⁸ esu) obtained at 1.54 μm is substantially larger than the value obtained at 1.907 μm (6200 × 10⁻⁴⁸ esu).

thiophene conjugating moiety and the stronger electron withdrawing ability of the tricyanovinyl acceptor. Extending the conjugation length in **8** by an ethylenic moiety results in **10**, and by a thienylvinyl moiety results in compound **11**. The extended conjugation present in these compounds caused further enhancement of the second-order nonlinearity. However, from the magnitudes of the $\beta\mu$ values (**10**, 9100×10^{-48} esu and **11**, 7400×10^{-4} esu), it may be concluded that olefinic units are more effective than thienylvinyl units in increasing molecular nonlinearity.⁹

In order to translate the molecular nonlinear responses into material responses, we have developed new synthetic methods to incorporate some of the above tricyanovinyl derivatives as pendant side-chains in various copolymers and the results will be reported elsewhere.¹⁰ Electrooptic studies of these compounds as guest materials in host polymer systems are also currently in progress.

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