

# Trends in Optical Nonlinearity and Thermal Stability in Electrooptic Chromophores Based upon the 3-(Dicyanomethylene)-2,3-dihydrobenzothiophene-1,1-dioxide Acceptor†

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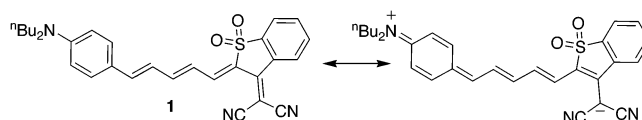
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A series of new thiophene-bridged chromophores based on the powerful heterocyclic acceptor 3-(dicyanomethylene)-2,3-dihydrobenzothiophene-1,1-dioxide has been synthesized; the dependence of the linear and second-order nonlinear optical properties and thermal stability of these species upon the donor group and the bridging group have been studied. In addition, the synthesis of a related new acceptor, not containing the fused benzene ring, is described and a chromophore based upon this acceptor is studied.

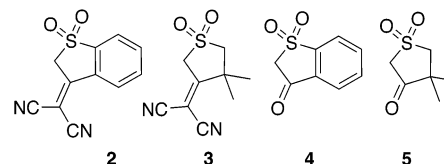
## Introduction

There has been tremendous interest in developing organic nonlinear optical (NLO) materials for a variety of electrooptic applications involving switching or modulation of light.<sup>1–6</sup> Materials with large second-order nonlinear susceptibility,  $\chi^{(2)}$ , and large electrooptic coefficient,  $r_{33}$ , are generally obtained by using electric fields to align polar second-order NLO guest chromophores above the glass-transition temperature,  $T_g$ , of a polymer host, in which they are dissolved, or to which they are covalently tethered; the alignment is “frozen in” once the polymer is cooled below  $T_g$ . The resulting  $\chi^{(2)}$  is dependent upon the chromophore’s first hyperpolarizability tensor,  $\beta$ , and upon the efficiency of alignment, which depends on its dipole moment,  $\mu$ ; a useful figure of merit is  $\mu\beta$ , the scalar product of  $\mu$  and the vectorial component of  $\beta$ . Structure–property relationships are now well-established for donor–acceptor chromophores;  $\beta$  can be related to the degree of ground-state polarization in the structure that itself depends on the electronic properties of donor, acceptor, and bridge. It has been shown that  $\beta$  is maximized for certain degrees of ground-state polarization, corresponding to specifically balanced contributions to the ground-state structure from “neutral” and “charge-separated” resonance structures (Figure 1) and to a specific reduction of bond-length alternation in a polyene bridging group.<sup>7–9</sup>

The temporal stability of the poling-induced alignment of the chromophores and of the guest–host mixture to phase separation is important for long-term device efficiency and is increased if high  $T_g$  (200–300 °C) host polymers are used; however, the chromophore must then be thermally stable at these temperatures to withstand the poling process. Increasingly, therefore, work



**Figure 1.** Structure of chromophore **1**, showing neutral (left) and charge-separated (right) resonance forms.



**Figure 2.** Structure of acceptors **2** and **3** and their respective parent ketones **4** and **5**.

on nonlinear optical chromophores has focused on increasing their thermal stability without adversely affecting their optical nonlinearities.<sup>10–21</sup>

We have reported the high- $\mu\beta$  chromophore **1** (Figure 1), based on the heterocyclic acceptor **2** (Figure 2),<sup>22,23</sup> and that a guest–host polymer system incorporating **1** as guest exhibited a high electrooptic coefficient of 55 pm V<sup>−1</sup>.<sup>24,25</sup> However, we found **1** to have poor thermal stability, in common with other polyene chromophores.<sup>12,26</sup> Various strategies have been used to improve polyene stability, including conformationally locking some or all of the double bonds of chromophores by their incorporation into ring systems<sup>27–37</sup> and replacing double bonds with aromatic groups. A benzene-1,4-diyl (*para*-phenylene, *p*-C<sub>6</sub>H<sub>4</sub>) bridging unit can be regarded as having the same effective conjugation length as a diene bridge. However, the ground-state polarization in species with these bridges is typically reduced relative to diene analogues because of the aromatic stabilization energy associated with the neutral resonance structure.<sup>38,39</sup> Thiophen-2,5-diyl bridging groups offer a compromise whereby the stability of the diene unit is increased by incorporation in a ring system, but where the ground-state polarization is less disrupted than with benzene-1,4-diyl bridging

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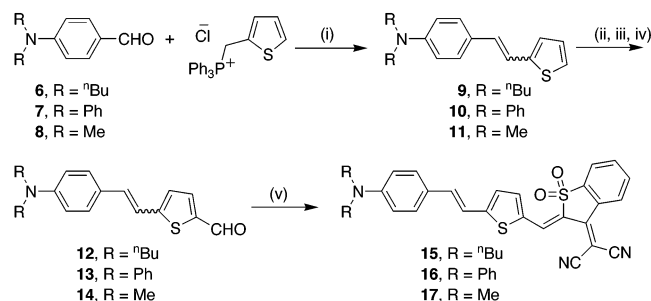
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## SCHEME 1



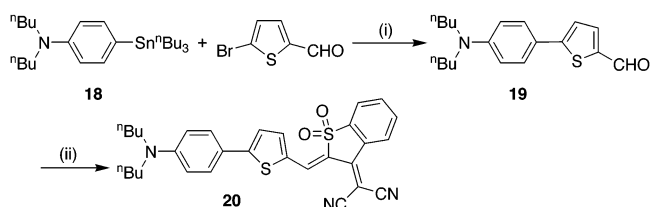
(i) Sodium ethoxide, ethanol, reflux; (ii) *n*-butyllithium, tetrahydrofuran; (iii) *N,N*-dimethylformamide; (iv) aq. HCl; (v) **2**, acetic anhydride, reflux or **2**, piperidine, methanol, reflux.

groups because of the lower aromaticity of thiophene. Hence, we also developed chromophore **15** (see Scheme 1), in which one of the double bonds of **1** is replaced with a 2,5-substituted thiophene, which has both larger  $\mu\beta$  and better thermal stability than **1**.<sup>24</sup> In this paper, we report more fully on **15** and a related series of new thiophene-bridged chromophores based on this powerful acceptor and on the trends in electronic properties (bond-length alternation, linear and nonlinear optical properties) and thermal stability observed with different donor and bridging groups. In addition, we also describe here the synthesis of a chromophore based upon a new acceptor, **3**, analogous to **2** but lacking the fused benzene ring and which acidity studies of the parent ketones **5** ( $pK_a = 5.83$ )<sup>40</sup> and **4** ( $pK_a = 7.65$ )<sup>41</sup> suggest may be a stronger acceptor (Figure 2); however, the authors of ref 40 did note that their  $pK_a$  value for **5** was anomalously low compared to that for other related structures and was possibly in error.

## Results and Discussion

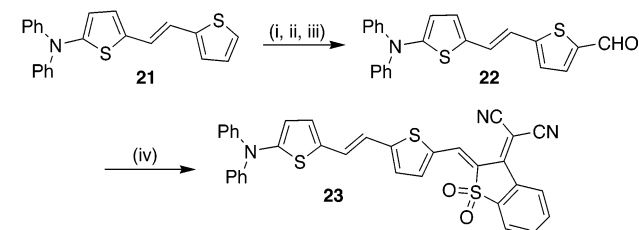
**Synthesis.** The (vinyl thiophene)-bridged chromophores (**15**–**17**) were synthesized according to Scheme 1. The Wittig reaction of the commercially available 4-(dialkylamino)benzaldehydes or of 4-(diphenylamino)benzaldehyde **7** (prepared from triphenylamine via a Vilsmeier reaction<sup>42</sup>) with thienylmethyl triphenylphosphonium chloride gave the corresponding styryl thiophenes **9**, **10**,<sup>43</sup> and **11**.<sup>44,45</sup> Lithiation of the styryl thiophenes (**9**–**11**), reaction with *N,N*-dimethylformamide, DMF, and subsequent hydrolysis afforded the corresponding aldehydes **12**, **13**, and **14**,<sup>46,47</sup> which were readily converted to chromophores **15**–**17** by Knoevenagel condensations with **2** under either basic (ethanol with piperidine catalyst) or acidic (acetic anhydride) conditions. The Wittig reaction gave mixtures of *E* and *Z* isomers; the aldehydes were also, therefore, obtained as mixture. However, the final chromophores were obtained as exclusively *E* isomers; we have observed similar isomerizations in other chromophore syntheses with rather strong acceptors. Presumably, in species with sufficiently strong acceptors, there can be substantial contributions to the ground-state structure from the charge-separated resonance structure, hence reducing the C=C character of the formal double bond and, thus, the barrier for isomerization.<sup>48</sup> The synthetic strategy for chromophore (**20**) with a single thiophene unit is outlined in Scheme 2. *N,N*-di-*n*-butyl-4-(tri-*n*-butylstannyl)aniline (**18**) was prepared from *N,N*-di-*n*-butyl-4-bromoaniline by lithiation and subsequent reaction with tri-*n*-butyltin chloride. Palladium-catalyzed coupling<sup>11</sup> of **18** with 5-bromothiophene-2-carboxaldehyde gave the corresponding aldehyde, **19**. Knoevenagel condensation of which with **2** in acetic anhydride yielded chromophore **20**. The diphenylaminothiophene-derived chromophore **23** was synthe-

## SCHEME 2



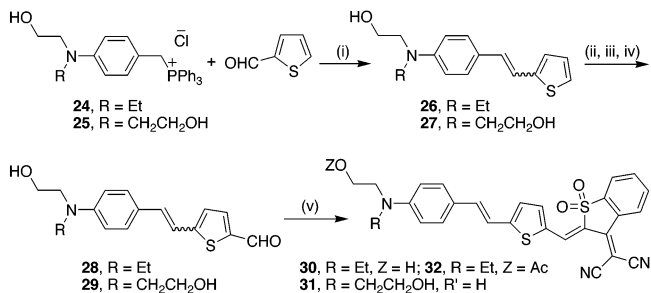
(i) Bis(triphenylphosphine)palladium dichloride, *N,N*-dimethylformamide; (ii) **2**, acetic anhydride, reflux.

## SCHEME 3



(i) *n*-Butyllithium, tetrahydrofuran; (ii) *N,N*-dimethylformamide; (iii) aq. HCl; (v) **2**, acetic anhydride, reflux.

## SCHEME 4



(i) Excess sodium ethoxide, ethanol, reflux; (ii) *n*-butyllithium, tetrahydrofuran; (iii) *N,N*-dimethylformamide; (iv) aq. HCl; (v) for **30** and **31** from **28** and **29**, respectively, **2**, pyridine, *n*-pentanol, reflux; for **32** from **28**, **2**, acetic anhydride, reflux.

sized as shown in Scheme 3; lithiation of the previously described compound **21**,<sup>15</sup> followed by reaction with DMF and subsequent hydrolysis afforded the aldehyde **22**. Knoevenagel condensation of which with **2** in acetic anhydride afforded chromophore **23**.

Hydroxyl-functionalized chromophores were synthesized as shown in Scheme 4. Phosphonium salts **24** and **25** were prepared according to literature procedures.<sup>49</sup> Wittig reaction of **24** and **25** with 2-thiophenecarboxaldehyde gave **26** and **27**, respectively. Direct lithiation of **26** and **27** with an additional one (for **26**) or two (for **27**) equivalents of *n*-butyllithium, reaction with DMF, and subsequent hydrolysis yielded aldehydes **28** and **29**. The hydroxyl functionalized chromophores **30** and **31** were readily obtained by Knoevenagel condensation of aldehydes **28** and **29** with **2** in refluxing *n*-pentanol in the presence of pyridine. When the Knoevenagel condensation of the aldehyde **28** with **2** was carried out in acetic anhydride, the O-acetylated chromophore **32** was the major product isolated.

The new acceptor **3** (Scheme 5) was synthesized by reaction of **5**<sup>50,51</sup> with malononitrile in absolute ethanol in the presence of anhydrous sodium acetate and was converted to chromophore **33** through Knoevenagel reaction with aldehyde **12**.

**Optical Properties.** The UV–visible absorption maxima,  $\lambda_{max}$ , absorptivities,  $\epsilon_{max}$ , oscillator strengths, *f*, and transition dipole moments,  $\mu_{ge}$ , for the new chromophores are summarized in Table 1. Values of  $\mu\beta$  were measured in dichloromethane

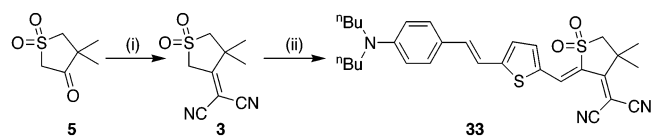
**TABLE 1: Optical Properties of the Chromophores in CH<sub>2</sub>Cl<sub>2</sub> (EFISH Determinations of  $\mu\beta$  at 1.907  $\mu$ M)**

cpd	$\lambda_{\max}$ /nm	$\epsilon_{\max}/\text{M}^{-1}\text{cm}^{-1}$	f	$\mu_{\text{ge}}/\text{D}$	$\mu\beta/10^{-48}\text{ esu}$	$\mu\beta(0)/10^{-48}\text{ esu}$	$\mu/\text{D}$	$\beta(0) 10^{-48}\text{ esu}$	$D\mu^a/\text{D}$
<b>1</b>	770				13500	3900			
<b>15</b>	742	61000	0.917	12.0	15000	4960	7.7	640	10.6
<b>16</b>	660	43000	0.772	10.4	5220	2320	5.6	410	8.1
<b>17</b>	704	35000	0.611	9.56	7800	3070			
<b>20</b>	704	48100	0.632	9.71	6650	2590			
<b>23</b>	738	42000	0.834	11.4	14500	4880			
<b>30</b>	708	46000	0.780	10.8	9870	3790			
<b>31</b>	688	41400	0.701	10.1	<sup>b</sup>	<sup>b</sup>			
<b>32</b>	702	55500	0.907	11.6	10380	4080			
<b>33</b>	720	33000	0.537	9.05	7,530	2730	8.2	330	10.3

<sup>a</sup> Calculated from  $\beta$ ,  $\lambda_{\max}$ , and  $\mu_{\text{ge}}$  using the two-level model. <sup>b</sup> EFISH measurements unreliable because of poor solubility of the chromophore.

**TABLE 2: Thermal Stability of Chromophores**

compound	normalized optical density (%)					
	time at 150 °C			time at 200 °C		
	10 min	30 min	60 min	10 min	30 min	60 min
<b>1</b>	87	59	21			
<b>15</b>	97	97	95	73	61	40
<b>16</b>	99	96	94	87	69	50
<b>17</b>	99	99	97	87	63	47
<b>20</b>	98	97	95	88	74	60
<b>23</b>	98	97	96	78	67	47
<b>30</b>	98	95	89	72	60	40
<b>31</b>	96	95	94	74	64	43
<b>32</b>	99	98	96	75	65	45
<b>33</b>	94	92	89	22	0	

**SCHEME 5**

(i) CH<sub>2</sub>(CN)<sub>2</sub>, sodium acetate, ethanol, reflux; (ii) **12**, acetic anhydride, reflux.

by electric-field-induced second-harmonic generation (EFISH).<sup>52,53</sup> The dispersion-corrected  $\mu\beta(0)$  values were estimated using the two-level model.<sup>54</sup> For chromophores **15**, **16**, and **33**, dipole moments,  $\mu$ , were also measured,<sup>55</sup> thus enabling us to estimate  $\beta(0)$  in these cases, and, hence, also to estimate  $\Delta\mu$ —the difference between ground-state excited-state dipole moments—using the two-level model ( $\beta(0) \propto \Delta\mu \cdot \mu_{\text{ge}}^2/E_g$ ).<sup>56</sup>

It can be seen that there is a significant reduction in nonlinearity upon replacing a diene bridging unit with a single thiophene bridge, as can be noted by comparison of the  $\mu\beta(0)$  values for chromophores **1** and **20**. This decrease is expected because of the decreased linear polarizability of the thiophene bridge, but there may also be contributions due to steric hindrance between hydrogen atoms on the thiophene and benzene rings leading to a nonplanar structure and further disrupting ground-state charge transfer. However, the  $\mu\beta(0)$  value of the (vinyl thiophene)-bridged chromophore, **15**, is actually larger than that of the polyene species **1**, with no adverse effects on transparency (**15** absorbs to the blue of **1**). However, **15** has an effective conjugation length greater than that of **1** by one double bond.

Examination of the (vinyl thiophene)-bridged chromophores, **15**–**17**, allows us to examine the role of the donor in this class of molecules. The linear spectra indicate a strong sensitivity of the electronic structure to donor strength; the bathochromic shift of  $\lambda_{\max}$  to lower energy seen from **16** to **17** to **15** suggesting increasing ground-state polarization and a donor strength sequence NPh<sub>2</sub> < NMe<sub>2</sub> < N<sup>n</sup>Bu<sub>2</sub>. The trend in  $\mu\beta(0)$  values

also points to ground-state polarization in the sequence **16** < **17** < **15**; the dipole moment data for **15** and **16** are also consistent. The functionalized NR(CH<sub>2</sub>CH<sub>2</sub>OH) chromophores, **30**–**32**, have similar linear optical properties to their NMe<sub>2</sub> analogue, **17**. The variation in  $\mu\beta$  values between **17**, **30**, and **32** presumably reflects the contributions of the effects of the dipoles associated with the OH and OAc groups to the molecular dipole moments.

Comparison of **16** with **23** shows that replacement of the phenylene group attached to the donor group with a *second* thiophene group leads to a dramatic red shift in the linear absorption and a dramatic increase in  $\mu\beta(0)$ . In fact, both the linear and nonlinear properties for **23** are similar to those for **15**. Thus, the adverse effects on ground-state polarization, and hence on  $\beta$ , engendered by replacing N<sup>n</sup>Bu<sub>2</sub> by the weaker NPh<sub>2</sub> donor, can be compensated for by replacing the phenylene between the donor and the bridge with the more polarizable thiophene bridge; similar observations have been made previously for similar tricyano-substituted chromophores.<sup>15</sup>

For the chromophore **33**, based on the new acceptor **3**, the nonlinearity is around half that of the analogous **2**-based chromophore **15**. The linear absorption band is moderately blue shifted, and the  $\Delta\mu$  value estimated from  $\mu\beta(0)$  is only slightly lower than that for **15**; however, the lower absorptivity of the linear absorption band reflects a value of  $\mu_{\text{ge}}^2$  only 60% of that of **15** and so presumably this factor is the most important contributor to the reduced  $\mu\beta(0)$ .

**Thermal Stability Studies.** Differential scanning calorimetry (DSC) provided little useful comparative information for these chromophores since decomposition was generally observed upon melting. Therefore, the thermal stability of the chromophores was examined by monitoring the decrease in absorbance at  $\lambda_{\max}$  for various compounds in 1-methylnaphthalene (a high-boiling solvent) at a given temperature, with no precautions taken to exclude air or exposure to ambient light. This approach assumes that the decomposition products do not show significant



absorbance at the chromophore's  $\lambda_{\text{max}}$ , which is reasonable since destruction of the donor, the acceptor, or the bridge would be anticipated to give a species lacking the low-energy charge-transfer band of the chromophore; moreover, previous studies have shown that the decomposition products of donor-acceptor chromophores do indeed lack low-energy absorption bands.<sup>57</sup> An analogous thermal bleaching of the polyene-bridged chromophore **1** was also carried out at 150 °C for comparison. As shown in Table 2, at 150 °C, all the thiophene-bridged chromophores underwent only about 10% or less decomposition over 60 min, whereas about 80% of polyene-bridged chromophore **1** decomposed under the same conditions. At 200 °C the thiophene-bridged chromophores based on acceptor **2** exhibited between 10% and 30% decomposition over 10 min, while the **5**-based chromophore **33** exhibited 80% decomposition and was totally destroyed within 30 min. The most stable chromophore is **20** in which there are no CH=CH bridging groups. In this particular experiment, any differences between the thermal stabilities of diarylamino donor-based species relative to their dialkylamino analogues appear to be small.

## Summary

A series of thiophene-containing chromophores based on the powerful heterocyclic acceptor **2** has been synthesized. Compared to the previously reported polyene-bridged chromophore **1** all of these species have considerably improved thermal stability; several of the new compounds have comparable or superior nonlinear optical properties to those of **1**, with no decrease in transparency (the new compounds all show absorptions blue-shifted relative to **1**). In this series, the optical and nonlinear optical properties are highly sensitive to the donor strength; however, the decreases in  $\mu\beta$  observed on replacing the di-*n*-butylamino donor with the diphenylamino donor can be compensated for by replacement of the phenylene unit adjacent to the donor with a second thiophene unit. Although there are few obvious trends in thermal stability among the new chromophores, it is likely that, in analogy with other work,<sup>37</sup> the photostability of the diphenylamino donor species is higher. Thus, chromophore **23** appears to be the most attractive candidate for electrooptic applications. The fused benzene ring of **2** clearly plays an important role in generating high optical nonlinearities; the main effect on  $\beta$  of replacing **2** with **3** in a chromophore is through dramatically decreasing the transition dipole term.

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**Supporting Information Available:** Experimental procedures and characterizing data for the chromophores. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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