

Thiazole and Thiophene Analogues of Donor–Acceptor Stilbenes: Molecular Hyperpolarizabilities and Structure–Property Relationships

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Abstract: We calculate the first hyperpolarizability (β) of several thiazole and thiophene analogues of donor–acceptor stilbene compounds using the ZINDO (sum-over-states) formalism. Because of the inherent dipolar nature of thiazole, in which C2 is electron-poor and C5 is electron-rich, the relative orientation of the thiazole subunit in the dipolar chromophore dramatically affects the nonlinear optical properties. In the “mismatched” case, the dipole of the thiazole ring opposes the molecular dipole created by the donor–acceptor substituents, while in the “matched” case, the dipole of the thiazole ring reinforces the molecular dipole. The hyperpolarizability of the “mismatched” monothiazole **2** ($\beta_{\mu} = 68 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) exceeds that of stilbene **1** ($\beta_{\mu} = 34 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) but is smaller than that of monothiophene **4** ($\beta_{\mu} = 90 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$). By contrast, the hyperpolarizability of the “matched” monothiazole **3** ($\beta_{\mu} = 177 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$) exceeds not only that of the “mismatched” monothiazole **2**, but also that of monothiophene **4**. Substituting thiazole for both aryl rings of stilbene produces very large hyperpolarizabilities in the “matched–matched” case (e.g., bis-thiazole **24**, $\beta_{\mu} = 254 \times 10^{-30} \text{ cm}^5 \text{ esu}^{-1}$). The nonlinear optical response of heterocyclic analogues of donor–acceptor stilbene derivatives is discussed in terms of the difference in aromatic delocalization energy between phenyl, thiophene, and thiazole, the electronic nature of the heteroaromatic rings, and conformational factors.

Introduction

Significant interest exists in the design and development of materials exhibiting large second-order nonlinear optical response^{1–3} because of the potential applications in telecommunications, optical computing, and optical signal processing.^{1,3–9} These applications require thermally robust materials with high nonlinear optical (NLO) response. Depending on the particular application, the use of organic materials may offer significant advantages over conventional inorganic crystals.¹ In the past decade, considerable effort focused on the development of organic materials with large molecular hyperpolarizabilities, improved optical transparency, and good thermal stability. Heteroaromatic compounds containing thiophene have attracted widespread interest because their linear and nonlinear optical properties are superior to those of the corresponding aryl analogues. Despite the growing interest in thiophene-containing NLO chromophores, a detailed understanding of the structure–property relationships for the closely related thiazole ring system is lacking.

We now present a systematic computational study of several heteroaromatic ring analogues of donor–acceptor stilbenes. Our results reveal that the relative orientation of a thiazole subunit in the dipolar chromophore dramatically affects the nonlinear optical properties. This effect provides the basis for the rational optimization of thiazole-containing NLO chromophores. In properly designed systems, the hyperpolarizabilities of thiazole-containing chromophores exceed those of their widely studied thiophene analogues.

Background

Typical organic NLO compounds include donor and acceptor moieties bridged by a π -conjugated linker.^{1,2,10–12} Bridging units such as polyenes, polyyenes, and aromatic rings are used in the majority of NLO chromophores. While polyenes and polyyenes allow for efficient charge transfer from donor to acceptor, their low thermal and chemical stabilities have driven researchers toward aromatic^{1,2,10–12} or tethered bridges.^{13–18} One of the early

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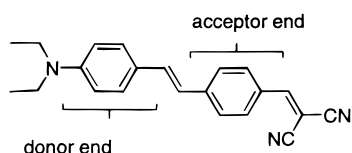
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bridging motifs was that of stilbene (e.g., compound **1**). Although the two aryl moieties of stilbene impart greater thermal stability than a donor–acceptor substituted polyene of equal length, the hyperpolarizability (β_{μ}) suffers dramatically. Replacement of one or both phenyl rings of stilbene with more easily delocalizable heteroaromatics has been studied both experimentally^{12,15,19–40} and computationally.^{41–44} In particular, thiophene derivatives have attracted widespread interest because their linear and nonlinear optical properties are superior to those of the corresponding aryl analogues.^{22–25,33,34,39,42,43}

Earlier studies of heteroaromatic systems (mainly thiophene, furan, and pyrrole) afforded three significant observations. First, increasing the electron density of the bridge enhances the hyperpolarizability.⁴² Second, substitution of a heteroaromatic ring for one of the aryl rings of stilbene typically has a different effect at the donor versus the acceptor end.^{42,44} Because of this, it is clear that differences in aromatic delocalization energies (ADE) must not be the only factors influencing the NLO properties for these systems. This leads to the third observation: the electron-rich or -poor nature of the heteroaromatic ring can influence the strength of the donor or acceptor through inductive effects.^{42,44}



In second-order NLO materials, charge transfer from donor to acceptor across a π -electron bridge disrupts the aromaticity

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
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Table 1. ZINDO Calculated π -Electron Charge Densities ($\rho(C)$)^a of Several Five-Membered Heterocycles

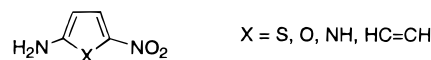


X	Y	$\rho(C2)$	$\rho(C5)$
NH	CH	-0.087	-0.087
O	CH	-0.051	-0.051
S	CH	-0.044	-0.044
S	NH	+0.135	-0.077

^a Negative values of $\rho(C)$ indicate an electron-excessive atom, and positive values of $\rho(C)$ indicate an electron-deficient atom.

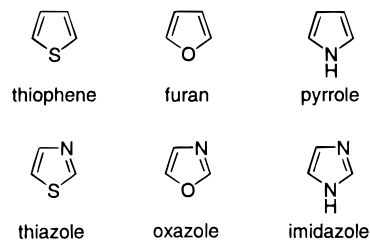
of the bridge. As the aromatic delocalization energy of the bridge decreases, the mixing of the ground state and charge-transfer state increases, leading to increased polarizability and hyperpolarizability. Another way to describe this effect is to say that, as the aromatic delocalization energy decreases, bond-length alternation across the bridge decreases. The aromatic delocalization energies (ADE) of benzene, thiophene, and thiazole are 36, 29, and 25 kcal/mol, respectively.⁴⁵ Hence, considerable interest has focused on thiophene and, to a lesser extent, on thiazole, as components of the π -electron bridge in organic NLO materials.

π -Electron densities at carbons C2 and C5 of pyrrole, furan, and thiophene are greater than benzene (Table 1).⁴⁴ Calculations of donor–heteroaromatic–acceptor chromophores show that



electron-rich heterocycles weakly withdraw electron density from the donor and strongly donate electron density to the acceptor. This has the effect of increasing the donor ability of the donor in the former case and decreasing the acceptor ability of the acceptor in the latter. The opposite effects are true for electron-poor heterocycles. Hence, electron-rich heterocycles have been referred to as auxiliary donors, and electron-poor heterocycles have been referred to as auxiliary acceptors.⁴⁴

Experiments and calculations of compounds incorporating five-membered aromatics with two heteroatoms such as thiazole,^{19,28–30,32,37,38,40,42,46} oxazole,^{30,32} and imidazole^{30,32,47}



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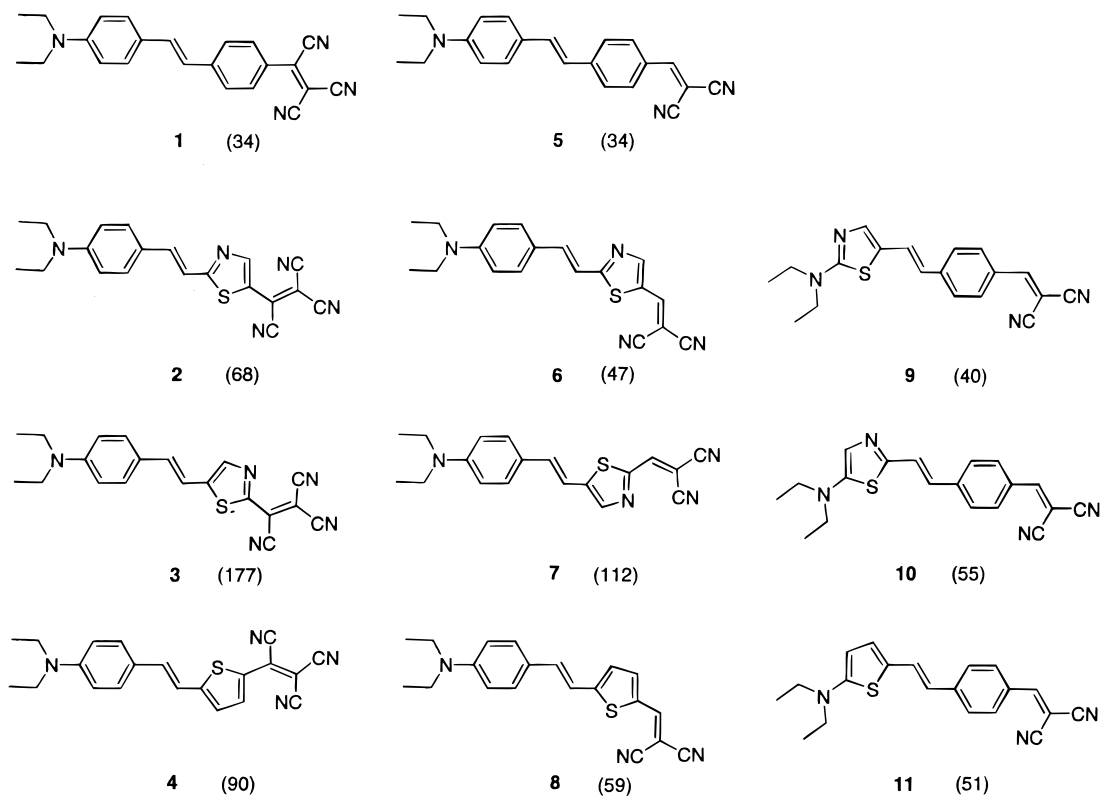
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Scheme 1^a

^a Numbers in parentheses are β_{μ} (1907 nm) in units of 10^{-30} cm⁵ esu⁻¹.

have shown that the incorporation of these ring systems into the π -electron bridge can enhance the hyperpolarizability significantly. When substituted at the acceptor end, thiazole enhances β to a greater extent than oxazole, which is better than imidazole.^{29,30,32,42} The opposite trend is observed for substitution at the donor end.

Computational Methods

Geometry optimizations were performed using the AM1 Hamiltonian in the MOPAC software package.⁴⁸ Each structure was verified as an energy minimum on the potential-energy hypersurface by calculation of the harmonic vibrational frequencies. For each compound, optimized geometries for 1–4 conformational isomers were investigated. In certain instances, “planar” structures were generated by rotation of the acceptor, aromatic rings, and ethylenic moiety of the optimized structures into a common plane. The spatial relationship of the amine moiety with respect to the adjacent aromatic ring was not altered. All data reported for “planar” compounds are derived from these nonoptimized structures. Frequency-dependent molecular hyperpolarizabilities (β) were computed at 1907 nm (0.65 eV) for the AM1 optimized geometries using the ZINDO (sum-over-states) program.⁴⁹ Hyperpolarizability data are reported in three formats: β , the total hyperpolarizability; β_{μ} , the component of hyperpolarizability in the direction of the dipole moment; and $\mu \cdot \beta$, the dot product of the dipole moment and hyperpolarizability vectors. The ZINDO sum-over-states methodology is considered reliable in predicting trends in hyperpolarizability, but the absolute magnitude of the computed hyperpolarizabilities should not be considered to be highly accurate.^{2,44}

(48) MOPAC version 6.0, Quantum Chemistry Program Exchange (QCPE #455), Department of Chemistry, Indiana University: Bloomington, IN.

(49) Frequency-dependent hyperpolarizabilities were computed from the AM1 geometries using the ZINDO sum-over-states program (1907 nm, summed over the lowest 45 excited states using single pair excitations from the highest 12 occupied orbitals into the lowest 12 unoccupied orbitals.) (ZINDO, version 96.0/4.0.0, Biosym/MSI: San Diego CA, 1996).

Table 2. ZINDO Calculated Electronic Absorption, Hyperpolarizability, and Dipole Moment for Compounds 1–11

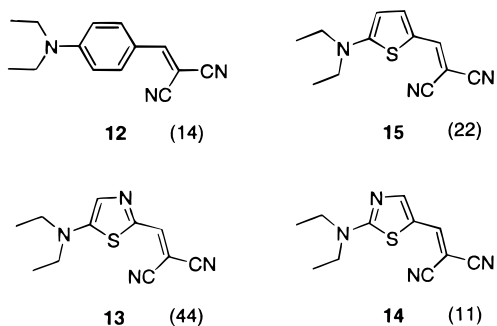
compound	λ_{\max}^a	$\mu \cdot \beta^{b,c}$	$\beta^{c,d}$	$\beta_{\mu}^{c,d}$	μ^e
1	371	275	35	34	8.1
2	443	756	68	68	11.1
3	497	1788	178	177	10.1
4	460	882	93	90	9.8
5	357	269	36	34	7.9
6	437	488	54	47	10.4
7	470	540	118	112	9.6
8	446	631	75	59	10.7
9	392	328	42	40	8.2
10	412	402	57	55	7.3
11	404	505	57	51	9.9

^a In units of nm. ^b In units of 10^{-48} cm⁶. ^c Evaluated at 1907 nm. ^d In units of 10^{-30} cm⁵ esu⁻¹. ^e In units of Debye (1 D = 10^{-18} cm esu).

Results and Discussion

Stilbene NLO Chromophores and Heterocyclic Analogues Containing One Thiophene or Thiazole Ring. The chromophores illustrated in Scheme 1 are derived from stilbene by replacing one aryl ring with either thiophene or thiazole. Two different electron acceptors, dicyanovinyl and tricyanovinyl, are shown. Table 2 contains the computed values of the electronic absorption maximum (λ_{\max}), molecular hyperpolarizability (β , β_{μ} , $\mu \cdot \beta$), and dipole moment (μ). For several compounds, up to four conformational isomers were calculated. The calculations predict minimal differences in the physical properties between conformational isomers (see below). Of this series, compounds **2**, **4**, **6**, and **8** have been synthesized and their hyperpolarizabilities have been measured.⁴⁶

The key findings revealed in Scheme 1 are: (i) thiazole derivatives display larger hyperpolarizabilities than their aryl analogues (cf. **2** and **3** vs **1**; **6**, **7**, **9**, and **10** vs **5**), (ii) the

Scheme 2^a

^a Numbers in parentheses are β_{μ} (1907 nm) in units of 10^{-30} cm⁵ esu⁻¹.

magnitude of the increase in hyperpolarizability depends substantially on the regiochemistry of the thiazole substitution (cf. **2** vs **3**; **6** vs **7**; **9** vs **10**), and (iii) in the matched case, hyperpolarizabilities of thiazole derivatives are not only larger than the aryl analogues, they are also larger than the thiophene analogues (cf. **3** vs **4**; **7** vs **8**; **10** vs **11**). As expected, the tricyanovinyl-substituted chromophores display larger hyperpolarizabilities than their dicyanovinyl analogues.^{11,12}

Incorporating a thiazole ring into a substituted stilbene derivative introduces two distinct elements of regiochemistry. Replacement of the aryl ring adjacent to the donor yields only a small increase in hyperpolarizability (cf. **9** or **10** vs **5**), and the relative orientation of the thiazole ring within the chromophore does not have a substantial effect (cf. **9** vs **10**). By contrast, replacement of the aryl ring adjacent to the acceptor affords a larger increase in hyperpolarizability (cf. **2** or **3** vs **1**; **6** or **7** vs **5**), and the relative orientation of the thiazole ring within the chromophore plays a crucial role in determining the hyperpolarizability (cf. **2** vs **3**; **6** vs **7**). When the dipole of the thiazole moiety reinforces the molecular dipole, as in the case of **3** and **7**, the hyperpolarizability is maximized.^{50–56} We refer to this situation as the “matched” case; conversely, we refer to **2** and **6** as “mismatched”. The hyperpolarizability for the series of thiazole–aryl chromophores increases in the order **9** (mismatched on the donor ring) < **6** (mismatched on the acceptor ring) < **10** (matched on the donor ring) < **7** (matched on the acceptor ring). The concept of matched and mismatched chromophores was investigated further by examining a set of simple donor–ring–acceptor compounds in which the ring is aryl, thiazole, and thiophene (Scheme 2; Table 3). Again, the hyperpolarizability of the matched chromophore **13** exceeds that of the mismatched chromophore **14** by a substantial margin (a

(50) The experimental dipole moments of thiazole^{51,52} and thiophene^{53–55} are shown below. The dipole moment of thiazole displays approximately equal components parallel and perpendicular to the direction of 2,5-disubstitution. The terms “matched” and “mismatched” are not intended to suggest that the dipole of the thiazole moiety is perfectly coincident with the overall molecular dipole.



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Table 3. ZINDO Calculated Electronic Absorption, Hyperpolarizability, and Dipole Moment for Compounds **12–15**

compound	λ_{\max}^a	$\mu \cdot \beta^{b,c}$	$\beta^{c,d}$	$\beta_{\mu}^{c,d}$	μ^e
12	335	119	16	14	8.5
13	439	365	46	44	8.3
14	383	92	13	11	8.4
15	407	227	26	22	10.3

^a In units of nm. ^b In units of 10^{-48} cm⁶. ^c Evaluated at 1907 nm. ^d In units of 10^{-30} cm⁵ esu⁻¹. ^e In units of Debye (1 D = 10^{-18} cm esu).

factor of 4). The only difference between this simple series and the substituted stilbenes is that the predicted hyperpolarizability for the mismatched thiazole (**14**) is slightly less than that of the aryl analogue (**12**).

The critical issue of thiazole regiochemistry (“matched” vs “mismatched”) has not been articulated previously. *Ironically, most of the thiazole-containing chromophores described in the literature represent “mismatched” cases.*^{19,28,29,32,40,46} Only the systems reported by Moylan,³⁰ Varanasi,^{42,57} and Wurthner^{37,38} correspond to “matched” cases.

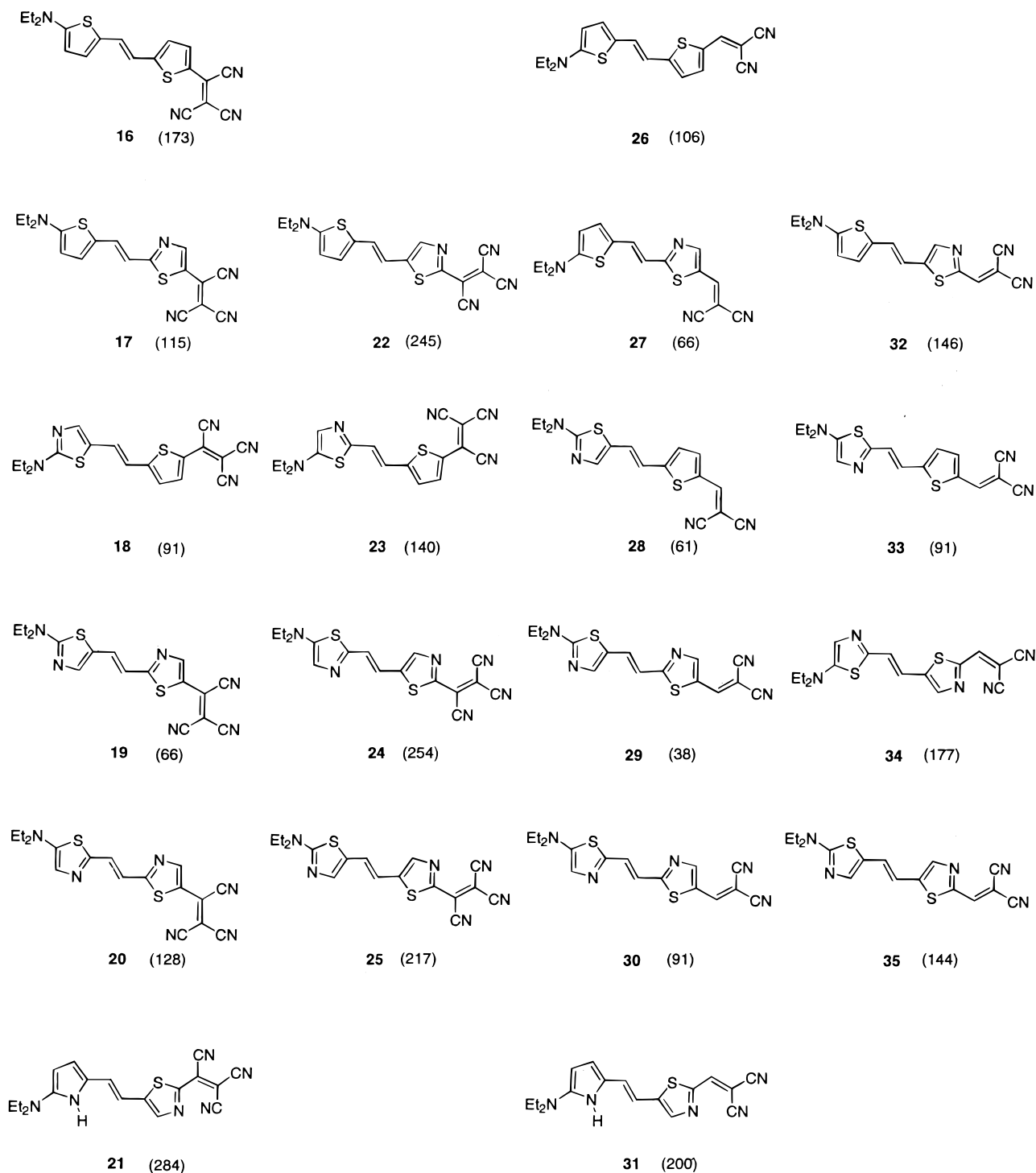
The concept of aromatic delocalization energy (ADE, see above) predicts that thiazole-substituted chromophores should show larger hyperpolarizabilities than thiophene, which in turn should be larger than aryl. Although our computational results are in accord with this behavior in certain instances (e.g., **7** > **8** > **5**), ADE cannot account for the differences that are observed when the same heteroaromatic ring is substituted adjacent to the acceptor (e.g., **7**, $\beta_{\mu} = 112 \times 10^{-30}$ cm⁵ esu⁻¹) or donor (e.g., **10**, $\beta_{\mu} = 55 \times 10^{-30}$ cm⁵ esu⁻¹). If ADE, in its simplest manifestation, was the sole factor determining the NLO response in these chromophores, no differences would be expected for **6** vs **9**, **7** vs **10**, and **8** vs **11**.

We look to differences in the π -electron density of C2 and C5 of thiazole to rationalize the predicted hyperpolarizabilities of the molecules described in Schemes 1 and 2. As shown in Table 1, the π -electron system of thiazole is electron-poor at C2 ($\rho(\text{C}2) = +0.135$) and electron-rich at C5 ($\rho(\text{C}5) = -0.077$).⁵⁸ Due to the polarized nature of the ring, thiazole offers the possibility of acting as both an auxiliary donor and acceptor. The results indicate that the electron-poor carbon (C2)/electron-rich carbon (C5) of thiazole affords larger hyperpolarizabilities when attached to the electron acceptor/electron donor substituent, respectively.

A second issue of regiochemistry concerns the predicted stronger effect on the hyperpolarizability when thiazole is adjacent to the electron acceptor (e.g., **7**) rather than adjacent to the electron donor (e.g., **10**). Previous computational studies showed that increasing the electron density of the bridge increases the hyperpolarizability⁴² and that bridging heterocycles enhance β_{μ} by serving as auxiliary donors or acceptors.⁴⁴ When thiazole is bonded to the acceptor at C2, as in compound **7**, it accomplishes both of these functions. The C2 carbon is electron-poor, acting as an auxiliary acceptor, while C5 is electron-rich and effectively adds electron density to the bridge. These two factors, working synergistically, afford enhanced NLO properties. Compound **7** is thus predicted to display an appreciable 2-fold enhancement of the hyperpolarizability relative to compound **10**. For compound **10**, the electron-rich C5 of thiazole acts as an auxiliary donor. The electron-deficient C2, however,

(57) Note that the molecular structure for compound **1f**—the molecule studied by Dirk et al.—is incorrectly depicted in the paper by Varanasi et al. The thiazole ring should have the opposite regiochemical orientation.

(58) We used the same methods as Albert et al. to compute the π -electron density at C2 and C5 for the heteroaromatics described in Table 1.

Scheme 3^a

^a Numbers in parentheses are β_{μ} (1907 nm) in units of 10^{-30} cm⁵ esu⁻¹.

decreases the electron density of the bridge. This works against the benefits of the auxiliary donor, C5. The resulting hyperpolarizability is smaller than that of **7**, although it is larger than both of the “mismatched” isomers (**6** and **9**).

Stilbene NLO Chromophores and Heterocyclic Analogues Containing Two Thiophene or Thiazole Rings. The chromophores illustrated in Scheme 3 are derived from stilbene by replacing both aryl rings with thiophene, thiazole, or pyrrole. Two different electron acceptors, dicyanovinyl and tricyanovinyl, are shown. Table 4 contains the computed values of the electronic absorption maximum (λ_{\max}), molecular hyperpolarizability (β , β_{μ} , $\mu\beta$), and dipole moment (μ). For several

compounds, up to four conformational isomers were calculated.⁵⁹ Once again, the calculations predict minimal differences in the physical properties between conformational isomers. Of this series, compounds **17**, **18**, **27**, and **28** have been synthesized, and their hyperpolarizabilities have been measured.⁶⁰

The key findings revealed in Scheme 3 are: (i) bis-thiophene, thiophene–thiazole, and bis-thiazole chromophores display larger hyperpolarizabilities than their diaryl (stilbene) analogues

(59) Data for the four computed isomers for compounds **3**, **4**, **8**, **17**, **18**, **27**, and **28** is supplied in the Supporting Information.

(60) Shu, C.-F.; Breitung, E. M.; McMahon, R. J., unpublished results.

Table 4. ZINDO Calculated Electronic Absorption, Hyperpolarizability, and Dipole Moment for Compounds **16–35**

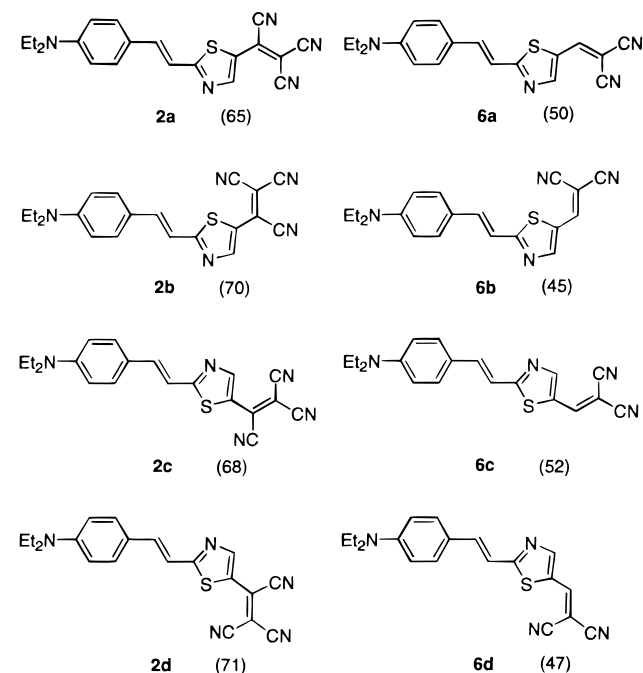
compound	λ_{\max}^a	$\mu \cdot \beta^{b,c}$	$\beta^{c,d}$	$\beta_{\mu}^{c,d}$	μ^e
16	515	2076	176	173	12
17	496	1553	117	115	13.5
18	484	1196	98	91	10.4
19	475	785	68	66	11.9
20	497	1498	132	128	11.7
21	552	2925	307	284	10.3
22	534	2671	249	245	10.9
23	512	1610	164	140	11.5
24	532	2515	259	254	9.9
25	531	2365	220	217	10.9
26	477	1155	107	106	10.9
27	478	792	78	66	12.0
28	478	720	79	61	11.8
29	456	429	40	38	11.3
30	479	965	93	91	10.6
31	515	1720	201	200	8.6
32	503	1562	168	146	10.7
33	466	801	92	91	8.8
34	505	1558	178	177	8.8
35	501	1397	148	144	9.7

^a In units of nm. ^b In units of 10^{-48} cm⁶. ^c Evaluated at 1907 nm. ^d In units of 10^{-30} cm⁵ esu⁻¹. ^e In units of Debye (1 D = 10^{-18} cm esu).

(cf. compounds in Scheme 3 vs **1** and **5**), (ii) the magnitude of the increase in hyperpolarizability depends substantially on the regiochemistry of the thiazole substitution (cf. **17** vs **22**; **27** vs **32**; etc.), and (iii) the large hyperpolarizabilities of “matched–matched” bis-thiazole derivatives exceed those of the “matched” thiophene–thiazole analogues, which, in turn, substantially exceed those of the bis-thiophene analogues (cf. **24** > **22** > **16**; **34** > **32** > **26**), and (iv) pyrrole–thiazole chromophores display the largest hyperpolarizabilities of their respective series (cf. **21** vs **24**; **31** vs **34**). Again, the tricyanovinyl-substituted chromophores display larger hyperpolarizabilities than their dicyanovinyl analogues.^{11,12}

Within a given family of thiophene–thiazole or bis-thiazole chromophores, the relative magnitudes of the hyperpolarizabilities can be rationalized by applying the principles gleaned from the preceding sections. In the thiophene–thiazole series, hyperpolarizabilities increase in the order **18** < **17** < **23** < **22** (tricyanovinyl acceptor) and **28** < **27** < **33** < **32** (dicyanovinyl acceptor)—exactly the same behavior as predicted for the thiazole–aryl chromophores (see above). The smallest hyperpolarizability occurs when thiazole is “mismatched” on the donor ring, and the largest hyperpolarizability occurs when thiazole is “matched” on the acceptor ring (cf. **18** vs **22**; **28** vs **32**). In the bis-thiazole series, hyperpolarizabilities increase in the order **19** < **20** < **25** < **24** (tricyanovinyl acceptor) and **29** < **30** < **35** < **34** (dicyanovinyl acceptor). The smallest hyperpolarizability occurs when thiazole is “mismatched–mismatched” (**19** and **29**), and the largest hyperpolarizability occurs when the thiazole is “matched–matched” (**24** and **34**). In the intermediate “matched–mismatched” cases, where one thiazole moiety reinforces the molecular dipole and the other opposes it (**20** vs **25**; **30** vs **35**), the large, favorable effect of having a matched thiazole on the acceptor ring (**25** and **35**) clearly dominates the modest, favorable effect of having a matched thiazole on the donor ring (**20** and **30**).

Calculations by Varanasi et al. establish that substitution of an electron-rich five-membered heteroaromatic moiety, such as pyrrole, at the donor end of an NLO chromophore enhances β significantly.⁴² Not only does pyrrole weakly withdraw electron density from the donor, it also adds electron density to the bridge. We therefore expected the combination of a donor-

Scheme 4^a

^a Numbers in parentheses are β_{μ} (1907 nm) in units of 10^{-30} cm⁵ esu⁻¹.

Table 5. Calculated Electronic Absorption, Hyperpolarizability, Dipole Moment, and Heat of Formation for Conformational Isomers of **2** and **6**

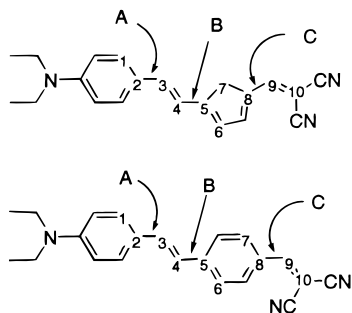
compound	λ_{\max}^a	$\mu \cdot \beta^{b,c}$	$\beta^{c,d}$	$\beta_{\mu}^{c,d}$	μ^e	ΔH_f^f
2a	442	676	65	65	10.4	193.6
2b	456	742	71	70	10.6	192.7
2c	443	755	68	68	11.1	192.3
2d	448	802	72	71	11.3	192.7
6a	435	570	52	50	11.4	155.5
6b	442	405	52	45	9.0	154.3
6c	433	593	54	52	11.4	154.2
6d	437	489	54	47	10.4	153.1

^a In units of nm. ^b In units of 10^{-48} cm⁶. ^c Evaluated at 1907 nm. ^d In units of 10^{-30} cm⁵ esu⁻¹. ^e In units of Debye (1 D = 10^{-18} cm esu). ^f In units of kcal mol⁻¹.

substituted pyrrole ring and an acceptor-substituted thiazole ring (in the matched arrangement) to produce a very large hyperpolarizability. Indeed, our calculations predict pyrrole–thiazole chromophores **21** ($\beta_{\mu} = 284 \times 10^{-30}$ cm⁵ esu⁻¹) and **31** ($\beta_{\mu} = 200 \times 10^{-30}$ cm⁵ esu⁻¹) to have the largest hyperpolarizabilities of their respective tricyanovinyl and dicyanovinyl series (cf. **21** vs **24**; **31** vs **34**). These compounds, along with **22**, **24**, and **25**, are predicted to display large hyperpolarizabilities ($\beta_{\mu} > 200 \times 10^{-30}$ cm⁵ esu⁻¹). Thus, our computations suggest that the incorporation of heteroaromatic rings, with careful consideration of electronic factors, can allow for significant enhancement of molecular NLO properties.

Conformational Effects. Four conformational isomers of compounds **2** and **6** are shown in Scheme 4. Most importantly, a comparison of the physical properties of the four isomers of **2** and **6** shows only subtle differences in λ_{\max} , β_{μ} , and μ (Table 5).⁶¹ The energy differences between isomers are relatively small. A similar analysis of conformational isomers for compounds **3**, **4**, **8**, **17**, **18**, **27**, and **28** (Schemes 1 and 3) shows

(61) Hutchings et al. report a similar comparison of four rotational isomers for two dicyanovinyl thiophene chromophores: Hutchings, M. G.; Ferguson, I.; McGeein, D. J.; Morley, J. O.; Zyss, J.; Ledoux, I. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1, 171.

Table 6. Calculated Hyperpolarizability and Dihedral Angles for Compounds 1–8

compound	$\beta^{a,b}$ opt	$\beta_{\mu}^{a,b}$ opt	$\beta^{a,b}$ planar	$\beta_{\mu}^{a,b}$ planar	$\angle A^{c,d}$ opt	$\angle B^{c,e}$ opt	$\angle C^{c,f}$ opt
1	35	34	58	57	162	164	137
2	68	68	78	78	174	176	147
3	178	177	178	177	175	178	180
4	93	90	114	109	169	175	147
5	36	34	44	40	164	159	146
6	54	47	54	47	176	180	180
7	118	112	118	112	178	180	180
8	75	59	77	60	167	177	180

^a In units of 10^{-30} cm⁵ esu⁻¹. ^b Evaluated at 1907 nm. ^c In units of degrees. ^d Defined by atoms 1–2–3–4. ^e Defined by atoms 3–4–5–6. ^f Defined by atoms 7–8–9–10.

that no single conformation is energetically favored by all of the compounds.⁵⁹ Even by restricting the comparisons to dicyanovinyl isomers or tricyanovinyl isomers, there seems to be no uniquely favored conformation within either series. Similarly, there seems to be no uniquely favored conformation within either series of thiophene- or thiazole-containing chromophores. A thorough conformational analysis of the bis-heteroaromatic chromophores would be a particularly complex undertaking because of the large number of conformations accessible to these unsymmetrical chromophores. Each molecule in Scheme 3 may display as many as $2^3 = 8$ low-energy conformations arising from the relative orientations of donor ring, acceptor ring, and cyanovinyl substituent. Although the structures shown in Schemes 1 and 3 may not necessarily represent the lowest-energy conformation for each chromophore, the results contained in Scheme 4, Table 5, and Supporting Information convince us that the conformational effects on the physical properties of the isomers will be small.

Not surprisingly, the π -electron frameworks computed for chromophores 1–35 display varying degrees of distortion from planarity. Key dihedral angles for compounds 1–8 are given in Table 6. Stilbene derivatives 1 and 5 display the largest deviations from planarity. The slightly differing geometric requirements of an aryl ring relative to a five-membered heterocyclic ring afford greater steric congestion between the C–H bonds of the aromatic ring and the proximal olefinic substituents. The seemingly surprising prediction that the tricyanovinyl- and dicyanovinyl stilbene derivatives 1 and 5 will show the same hyperpolarizability is understood in terms of the larger deviation from planarity by the tricyanovinyl compound 1 (dihedral $\angle C$, Table 6). This steric interaction effectively decreases the hyperpolarizability. Indeed, enforcing planarity on structures 1 and 5 yields the expected result of a larger hyperpolarizability for the tricyanovinyl derivative 1 (Table 6).⁶² Hence, based on purely steric issues, larger

(62) In generating the “planar” structures from the optimized structures, the position of the diethylamine moiety with respect to the adjacent aromatic ring was not altered. The dihedral angles not associated with the amine are $180^\circ \pm 1^\circ$.

nonlinearities are expected for stilbene analogues in which both aryl rings are replaced with heteroaromatic rings. To assess the deviations from planarity on the NLO response of thiophene and thiazole chromophores, the hyperpolarizabilities for both optimized and planar structures of 2–4 and 6–8 were computed (Table 6). In general, the distortions from planarity are less severe than for the stilbene analogues 1 and 5, and the consequence of these distortions on the hyperpolarizability is modest. Notably, when a heteroaromatic ring is present at the acceptor end of the molecule, the central alkene moiety and the heteroaromatic ring are nearly coplanar ($\angle B = 178 \pm 3^\circ$ for 2–4 and 6–8). Compounds containing a tricyanovinyl substituent display the most severe distortions from planarity ($\angle C = 137$ – 147° for 1, 2, 4) except in the “matched” thiazole case ($\angle C = 180^\circ$ for 3, 21, 22, 24, 25). This favorable conformation may arise because of the absence of a C–H bond at the 3-position of the heterocycle.

Summary

In an effort to better understand the nonlinear optical properties of heteroaromatic analogues of donor–stilbene–acceptor compounds, we utilized the ZINDO (sum-over-states) methodology to compute molecular hyperpolarizabilities (β). Due to the unsymmetrical nature of thiazole, bonding to the donor or acceptor through either C2 or C5 affords molecules with disparate nonlinear optical properties. Because of its electron-rich (C5) and electron-poor (C2) positions, thiazole can act as both an auxiliary donor and acceptor. Compounds that take advantage of this property, in which the dipole of the thiazole moiety reinforces the molecular dipole (“matched” case), show very large hyperpolarizabilities—often exceeding those of their thiophene analogues. Thiazole derivatives 21, 22, 24, 25, and 31 show the greatest potential as NLO chromophores, displaying hyperpolarizabilities up to 8 times the stilbene derivative with the same donor–acceptor substitution. In addition to electronic factors, it is clear that steric factors also play an important role. In most instances, heterocyclic rings enable the attainment of planar, or nearly planar, geometries, which translates into larger hyperpolarizabilities.

The differences in NLO response between compounds containing aryl, thiophene, and thiazole rings are not accountable through differences in their aromatic delocalization energies. The fact that substitution of the same heteroaromatic ring adjacent to the donor does not have the same effect on the nonlinear optical properties as substitution at the acceptor end demonstrates the inadequacy of the ADE analysis.

Our computations suggest that the incorporation of thiazole into nonlinear optical chromophores, with careful consideration of steric and electronic factors, can allow for significant enhancement of hyperpolarizability relative to either aryl or thiophene analogues.

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Supporting Information Available: The linear (λ_{\max}) and NLO response (β_{total} , β_{μ}), dipole moment (μ), and heat of formation (ΔH_f) for four conformational isomers of compounds 3, 4, 8, 17, 18, 27, and 28 (PDF file). Cartesian coordinates (in Å) for AM1 geometries of compounds 1–35 (ASCII file). This material is available free of charge via the Internet at <http://pubs.acs.org>.