

Synthesis and Characterization of Nonlinear Optical Chromophores with Conformationally Locked Polyenes Possessing Enhanced Thermal Stability

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Dipolar NLO chromophores with an interposed conjugated tetraene segment in which all but four of the methine groups are incorporated into a tetrahydronaphthalene framework have been synthesized and characterized. This conformation-locking approach furnishes NLO chromophores possessing an enhanced thermal stability. X-ray crystallographic data indicate that the polyenic chain of these molecules exhibits a near-planar all-trans conformation in the solid state. EFISH measurements show that these conformationally locked tetraenic chromophores exhibit large second-order optical nonlinearities ($\mu\beta \sim 4000 \times 10^{-48} \text{ cm}^6$ at 1907 nm), although the nonlinearities of the corresponding "unlocked" analogues are slightly larger.

Introduction

The growing interest in organic materials for electrooptic device applications has led to the development of NLO chromophores possessing large molecular second-order nonlinearity (β).^{1,2} Most attempts to design chromophores with large β have been based upon "push-pull" compounds. Such chromophores are generally represented as D- π -A, where the electron-donor (D) and electron-acceptor (A) groups are linked by a π -conjugated bridge.³ In such chromophores, the donor and

acceptor substituents provide the requisite ground-state charge asymmetry, whereas the π -conjugation moiety provides a pathway for the redistribution of electric charges under the influence of electric fields. These molecules exhibit a large hyperpolarizability (β), owing to the occurrence of an intramolecular charge-transfer transition. Unhindered by aromaticity, polyenes provide the most effective pathway for efficient charge delocalization between donor and acceptor groups and are often used as bridging π -conjugated units to optimize β .⁴ The simple polyenes, however, are not sufficiently thermally stable to be used for device applications.⁵ In poled E–O polymer systems, the polar alignment is preserved either by using host polymers

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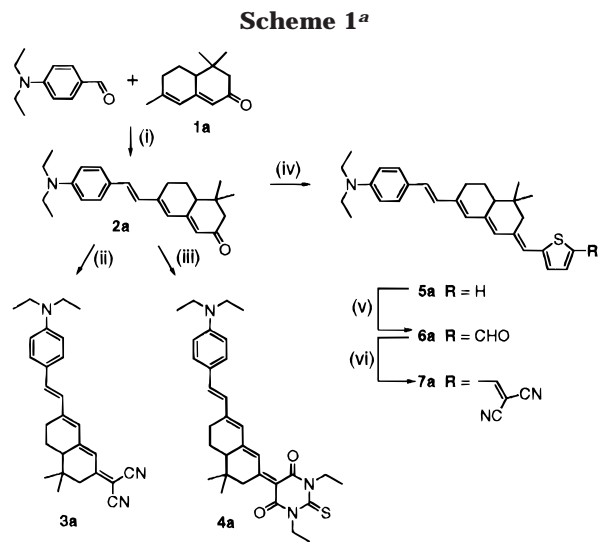
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with high glass transition temperatures (200–300 °C), or by cross-linking the chromophore–polymer composite. In either case, it represents a challenge to chemists in this field to develop highly nonlinear chromophores with thermal stabilities exceeding 250 °C, to survive the materials processing and device fabrication conditions.

Incorporating a polyene chain into a ring system to improve the photostability of a dye has been reported previously.⁶ Precedent for the use of conformationally locked polyenes in organic photorefractive materials to provide thermal and photochemical stability has also been reported by Marder and co-workers.⁷ Recently, we⁸ and others^{9,10} have shown that additional thermal stability can be added to NLO chromophores by incorporating part or all of a methine chain into a ring system. In this report, we extend this approach to NLO chromophores with an interposed conjugated tetraene segment in which all but four of the methine groups are incorporated into a tetrahydronaphthalene framework. Here, we report on the synthesis, electronic absorption spectra, X-ray crystal structures, and second-order nonlinear optical properties of the conformationally rigid NLO chromophores as well as their nonrigid analogues. We also demonstrate that the conformational-locking approach leads to an enhancement in the molecular thermal stability.

Results and Discussion

Synthesis. The synthetic route for the preparation of the conformationally locked NLO chromophores is shown in Scheme 1. The key intermediate 4,4,7-trimethyl-2,3,4,4a,5,6-hexahydro-2-naphthalenone, compound **1a**, was prepared according to the reported procedure.¹¹ With isophorone used as the starting material, the enone was converted to the enol acetate by acid-catalyzed (*p*-toluenesulfonic acid) exchange with isopropenyl acetate. Diels–Alder reaction of the enol acetate with methyl vinyl ketone, followed by saponification and retro-aldolization in CH₃ONa/CH₃OH, gave compound **1a**. Knoevenagel condensation of 4-(diethylamino)benzaldehyde with **1a** in the presence of *t*-BuOK/*t*-BuOH yielded compound **2a**. Knoevenagel condensation of compound **2a** with malononitrile or 1,3-diethyl-2-thiobarbituric acid resulted in the formation of compounds **3a**⁹ and **4a**, respectively. Wittig–Horner condensation of compound **2a** with 2-thiophenemethyl phosphonate in *t*-BuOK/THF afforded compound **5a**. Compound **5a**, which lacks an electron-withdrawing group at the end of its conjugated moiety, was lithiated with *n*-BuLi and subsequently quenched with *N,N*-



^a Reagents: (i) *t*-BuOK/*t*-BuOH; (ii) CH₂(CN)₂; (iii) diethylthiobarbituric acid; (iv) diethyl 2-thienylmethylphosphonate; (v) *n*-BuLi, DMF; (vi) CH₂(CN)₂.

dimethylformamide to give the formyl derivative **6a**. A further Knoevenagel reaction of compound **6a** with malononitrile led to the dicyanovinyl-substituted chromophore **7a**. All compounds were characterized using conventional spectroscopic techniques. For compounds **2a**–**7a**, the segment of the polyene chain that is not conformationally locked retains an *s*-trans configuration as established by analysis of the ¹H NMR coupling constants ³*J* = 15.9–16.2 Hz. Definitive confirmation of the all-trans stereochemistry of compounds **3a** and **7a** was provided by X-ray analysis (see below).

To compare thermal stabilities, the analogous NLO chromophores containing a simple, conformationally flexible tetraenic segment with an all-trans configuration were also prepared. Reaction of 4-(diethylamino)phenyllithium, which was generated from lithium–halogen exchange of *n*-BuLi with 4-(diethylamino)phenyl bromide, with 7-(*N,N*-dimethylamino)-hepta-2,4,6-trienal (**1b**)¹² gave compound **2b**. With compound **2b** used as the starting material, and by utilizing the synthetic strategy for the preparation of the cyclic analogues, the corresponding acyclic NLO chromophores were prepared, as shown in Scheme 2. As the π -conjugated chain increases, the solubility of the chromophore becomes poor. The spectroscopic characterization of the diethyl analogue of compound **7c** was limited by its poor solubility. The dibutyl groups of compound **7c**, which impart greater solubility, were incorporated using 4-(dibutylamino)phenyl bromide as the starting material in the synthetic procedure. The conformationally locked chromophores have better solubility than the “unlocked” chromophores as a result of the incorporation of dimethyl-disubstituted fused rings.

Electronic Absorption Spectra. The electronic absorption spectra of the push–pull polyenes investigated in the present work display an intense, broad low-energy band attributed to an intramolecular charge-transfer (CT) transition (Table 1). The CT bands shift bathochromically with increased acceptor strength. The

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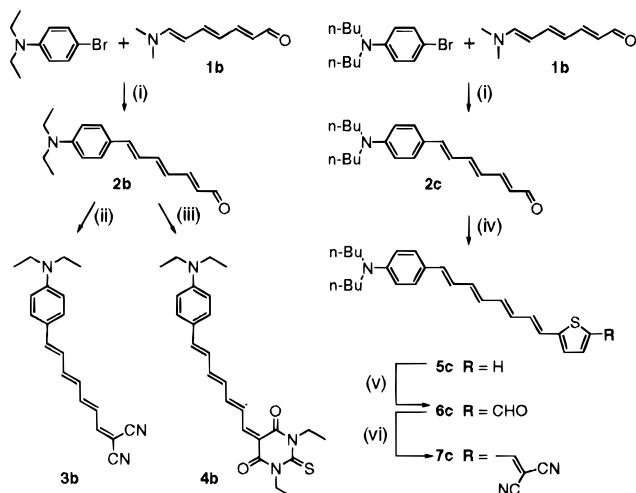
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Scheme 2^a

^a Reagents: (i) *n*-BuLi/THF; (ii) CH₂(CN)₂; (iii) diethylthiobarbituric acid; (iv) diethyl 2-thienylmethylphosphonate; (v) *n*-BuLi, DMF; (vi) CH₂(CN)₂.

Table 1. Electronic Absorption, Decomposition Temperature, Dipole Moment, and EFISH Data for Compounds 3a–7c

compound	λ_{\max} , ^a nm	T_d , °C	$\mu^{b,c}$ calc	$\mu \cdot \beta^{a,d}$ expt	$\beta_{\mu}^{a,e}$ expt
3a	538	317	10.3	3880 ^f	378
3b	563	170	9.8	4440	453
4a	619	252			
4b	644	174			
7a	609	252	10.5	4510	432
7c	592	200	10	5210	518

^a In CHCl₃. ^b In units of Debye (1 D = 10⁻¹⁸ cm esu). ^c Computed from AM1 geometry. ^d In units of 10⁻⁴⁸ cm⁶. ^e In units of 10⁻³⁰ cm⁵ esu⁻¹. ^f $\mu \cdot \beta = 3230 \times 10^{-48}$ cm⁶ determined by EFISH at 1600 nm in Me₂SO, ref 9.

addition of a thiophene ring into the π -conjugating system also induces a bathochromic shift in the CT band. When compared to the corresponding simple tetraenic chromophores **3b** and **4b**, the conformationally locked chromophores **3a** and **4a** have blue-shifted CT bands. A comparison of absorption spectra for compounds **7a** and **7c**, however, shows that the conformationally locked chromophore **7c** has a red-shifted CT band. In the trienic system, similar results were observed.^{8a}

Thermal Stability. The thermal stability of these chromophores was initially studied by differential scanning calorimetry (DSC, 10 °C/min). The intercept of the leading edge of the thermal decomposition exotherm by the baseline of each DSC scan was assigned as the decomposition temperature (T_d).^{5a,13} It should be noted that T_d values only provide a helpful upper limit of thermal stability. The T_d 's of the chromophores investigated are shown in Table 1. Comparison of the T_d 's of conformationally locked, tetraenic NLO chromophores, **3a**, **4a**, and **7a**, with those of corresponding simple tetraenic chromophores, **3b**, **4b**, and **7c**, reveals that the conformation-locking method provides a dramatic enhancement of molecular thermal stability. The enhancement of thermal stability is attenuated as the π -conjugated system of the NLO chromophore is ex-

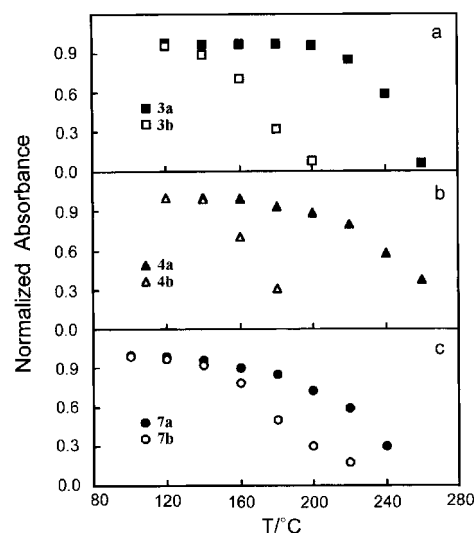


Figure 1. Thermal stability of **3a**, **3b**, **4a**, **4b**, **7a**, and **7c**, respectively, heated isothermally on glass substrates at various temperatures for 20-min intervals, measured by following the change in absorbance of a 2 wt % dye-doped polyquinoline thin film vs temperature.

tended by adding a thiophene ring (Table 1). Comparison of the T_d 's of **3b** and the thiophene-containing chromophore, **7c**, indicates that the addition of a thiophene ring to the tetraenic π -system leads to an increase of molecular thermal stability. In contrast, a reduction in thermal stability is observed when a thiophene ring is introduced into the π -system of the conformationally locked tetraene (**3a** vs **7a**).

The T_d 's of **3b**, **4b**, and **7c** are close to the melting points (T_m), and the T_d 's obtained from DSC may not reflect the thermal behavior for chromophores in the polymer system where the NLO chromophores will be used for device applications. Therefore, we examined the thermal stability of the chromophores in polyquinoline (PQ-100, Maxdem) films.^{8a,c} Polyquinoline thin films containing 2 wt % chromophore were heated isothermally on glass substrates at various temperatures for 20-min intervals. The π - π^* charge-transfer absorption band of the chromophore was used to monitor the decomposition temperature. The change in the absorption maximum of the CT band at various temperatures was determined, and the results are shown in Figure 1. The thermal stabilities evaluated for chromophores within the polymer system again demonstrate that the conformationally locked polyenes possess enhanced stability, which is consistent with the data obtained from DSC measurements. The absorbances of the polymer film containing conformationally locked chromophore **3a** started diminishing at 240 °C, somewhat lower than expected from the DSC measurement (T_d = 317 °C). This may be due to the sublimation of the chromophore out of the polymer matrix through the uncovered side of the sample cell at the temperature near the glass transition temperature of polyquinoline (250–260 °C).¹⁴

X-ray Molecular Structures. The molecular structure of compounds **3a**, **7a**, **3b**,^{8c} and **7c** in the solid state

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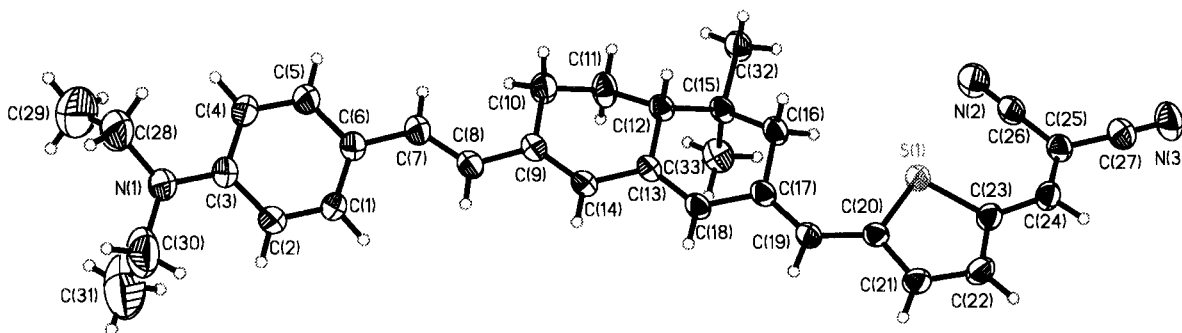


Figure 2. ORTEP view of compound 7a.

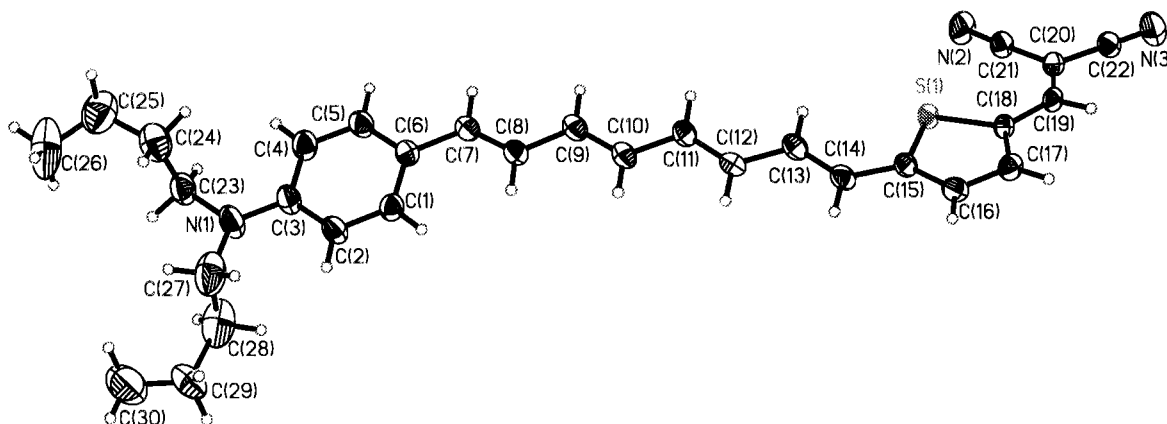


Figure 3. ORTEP view of compound 7c.

Table 2. X-ray Structural Data of Complexes 7a and 7c

compound	7a	7c
formula	C ₃₃ H ₃₅ N ₃ S	C ₃₀ H ₃₃ N ₃ S
mol wt	505.70	467.55
crystal system	monoclinic	triclinic
space group	P2 ₁ /n	Pī
a, Å	9.0071(1)	6.7241(1)
b, Å	23.1286(2)	11.9079(1)
c, Å	13.8990(1)	17.2504(1)
α, deg	90	79.979(1)
β, deg	96.949(1)	88.404(1)
γ, deg	90	89.247(1)
volume, Å ³	2874.19(5)	1359.59(2)
Z	4	2
D _c , g/cm ³	1.169	1.142
F(000)	1080	500
2θ (max)	50.06°	50.06°
h k l ranges	−10 10, −27 22, −16 16	−8 8, −14 14, −20 20
crystal size, mm	0.40 × 0.15 × 0.08	0.40 × 0.30 × 0.20
μ(Mo Kα), mm ^{−1}	0.138	0.141
transmission:	0.9280, 0.6363	0.9562, 0.6167
max, min		
independent reflections (R _{int})	5087 (0.0468)	4786 (0.1128)
no. of parameters	335	308
final R indices:	0.0683, 0.1407	0.1049, 0.2250
R1, wR2		
G.O.F.	1.027	1.019
D-map, max/min, e/Å ^{−3}	0.408/−0.213	0.452/−0.331

were determined by X-ray crystallography. Table 2 shows the crystallographic data for compounds 7a and 7c. The molecular structures of compounds 7a and 7c are illustrated in Figures 2 and 3. The most noticeable feature is that the polyenic chains of these molecules exhibit a nearly planar all-trans conformation. The phenyl ring of the donor moiety is slightly twisted (twist angle $\approx 8^\circ$ for 3a, 11° for 3b, 22° for 7a, and 4° for 7c) with respect to the plane of the polyenic chains. For compounds 3a and 3b, the dicyanovinyl acceptor lies

close to the plane of the conjugated chain (twist angle $\approx 9^\circ$ for 3a and 11° for 3b). The thiophene ring in compound 7a is approximately coplanar with the polyenic chain (twist angle $\approx 1^\circ$), and the thiophene ring in compound 7c is tilted 19° with respect to the plane of polyenic chain. The dicyanovinyl acceptor twists with respect to the thiophene ring by 9° for compound 7a and by 4° for compound 7c. Bond length alternation (BLA), defined as the difference between the average length of carbon–carbon double and single bonds in the polyenic chain linking the donor and acceptor groups, is a structural parameter developed for examining structure–property relationships for NLO chromophores.¹⁵ The BLA values of 3a and 3b are 0.082 and 0.069 Å, respectively, which are smaller than that of unsubstituted octatetraene, 0.12 Å.¹⁶ This result indicates a moderate contribution of the charge-separated resonance form in the ground state of molecules 3a and 3b in the solid state. The BLA values of 7a and 7c, in which the π -conjugated bridges are extended by adding a thiophene ring, are 0.102 and 0.101 Å, respectively. The increase of BLA values with increasing π -conjugation length is a consequence of the larger energetic price associated with charge separation in extended π -systems. This reflects the growing difficulty of separating

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charges over larger distances. Such behavior has been observed with other series of push–pull polyenes.¹⁷

Nonlinear Optical Properties. The nonlinear optical properties of compounds **3a**, **3b**, **7a**, and **7c** were determined experimentally by electric-field-induced second-harmonic generation (EFISH) (Table 1).¹⁸ The values of the dot product $\mu \cdot \beta$ were measured at 1907 nm in chloroform. AM1-optimized geometries were used to compute dipole moments,¹⁹ which enabled the determination of β_{μ} , the hyperpolarizability in the direction of the dipole moment.

The measured values of $\mu \cdot \beta$ for **3a**, **3b**, **7a**, and **7c** are quite large $[(3800\text{--}5200) \times 10^{-48} \text{ cm}^6 \text{ at } 1907 \text{ nm}]$ (Table 1) and are in good accord with values reported for similar donor–acceptor-substituted polyenes.^{4,9,10} EFISH experiments show that conformationally locked compounds (**3a** and **7a**) have slightly smaller hyperpolarizabilities (β_{μ}) than their simple nonrigid analogues (**3b** and **7c**). The differences in the hyperpolarizabilities for the rigid and nonrigid chromophores **3a** and **3b** can be rationalized in terms of the structural data obtained by X-ray crystallography. The bond-length alternation parameter indicates a polyenic ground-state electronic structure for **3a** (BLA = 0.082 Å) and an increased contribution from the charge separated resonance form for **3b** (BLA = 0.069 Å). Previous studies concerning the relationship of β vs BLA predict an increase in β as the BLA decreases from approximately 0.1 to 0.05 Å.⁴ The behavior of compounds **7a** and **7c**, however, cannot be rationalized through differences in BLA parameters. Conformational factors are likely the cause for the lower hyperpolarizability of **7a**, relative to **7c**, and may also

play a role in the differences between **3a** and **3b**. The population of conformational isomers that is probed during the EFISH measurement on solution is not well-represented by the crystallographic data. Because of the complexity of these issues, further structure vs nonlinear optical property relationships will be discussed in a future publication.

Conclusions

We have developed a synthetic methodology for obtaining dipolar NLO chromophores with an interposed conjugated tetraene segment in which all but four of the methine groups are incorporated into a tetrahydronaphthalene framework. The data from X-ray crystallography reveal that the polyenic chain of these molecules exhibits a near planar all-trans conformation. The conformationally locked tetraenic chromophores possess enhanced thermal stability and efficient, but slightly smaller, second-order optical nonlinearity, compared with their “unlocked” counterparts. This study demonstrates that by using the conformation-locking approach a tradeoff between the molecular nonlinearity and the thermal stability can be achieved. To translate the molecular nonlinear responses into bulk material responses, we have developed synthetic methods to incorporate some of the conformationally locked NLO chromophores as pendant side chains in aromatic polyquinolines; the results will be reported elsewhere.

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Supporting Information Available: Experimental details including general methods, synthesis procedures, X-ray crystallography, and NLO measurements, as well as ORTEP view for compound **3a** and X-ray crystallographic data for compounds **3a**, **7a**, and **7c**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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