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Synthesis and Nonlinearity of Triene Chromophores Containing the Cyclohexene Ring Structure

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A series of conjugated donor−acceptor trienes in which the central double bond is incorporated into an unsaturated isophorone, verbenone, or chromone ring has been synthesized. In each case, the donor group consists of an amine and an aromatic or heterocyclic ring system, and the acceptor is the dicyanomethylidene group. The nonlinear optical properties of each of the compounds has been measured and correlated with its structure. The dipole moments and molecular hyperpolarizabilities of these compounds, like those of other conjugated polyenes, are large enough to be used as the active components of electrooptic polymers. Unlike other donor−acceptor polyenes, however, these compounds exhibit the thermal stability required for such applications.

Introduction

A major challenge in the design of nonlinear optical chromophores for electrooptic (EO) devices is simultaneously achieving acceptable thermal stability, transparency, nonlinearity, and processability in one compound. Thermal stability is typically enhanced by incorporating aromatic rings into the delocalized bridge between the electron-donating and -accepting groups, but it has been shown that such substitution produces excited states that feature quinoidal bonding patterns in those rings and concomitant loss of aromaticity.[1] The first excited state in such compounds is thus energetically disfavored, decreasing the hyperpolarizability β. The nonlinearity can be enhanced to some extent by incorporating quinoidal and aromatic rings into the bridge in pairs, so that the net aromatic stabilization energy upon excitation is close to zero, but the thermal stabilities of such compounds will be compromised. This nonlinearity−stability tradeoff can be evaded to some extent by using aromatic substitution upstream of the electron-donor group only.[2] This substitution pattern is especially effective when combined with cyanomethylene acceptor groups.[3] Nevertheless, the largest measured molecular hyperpolarizabilities have been found in long conjugated polyene systems with few or no aromatic rings between the donor and the acceptor.[4] Unfortunately, such compounds decompose far below the 300 °C required for incorporation into real devices[5] and are sufficiently red-shifted as to fail the transparency requirements. One class of compounds has been found to evade the nonlinearity−transparency tradeoff somewhat by featuring two low-lying excited states that contribute to β in an additive manner,[6] but other systems with that desirable quality remain to be found. Accordingly, it remains of great interest to determine whether the thermal stabilities of unsaturated delocalized systems are irretrievably low or whether structural modifications can increase decomposition temperatures without decreasing hyperpolarizabilities proportionally.

The work described in this paper was initially motivated by success using the laser dye 4-(dicyanomethylene)-2-methyl-6-(*p*-dimethylaminostyryl)-4*H*-pyran (DCM) in the development of an all-polyimide integrated process for electrooptic waveguides in 1991.[7] In an effort to extend this work, we embarked upon the design, synthesis, and characterization of a series of chromophores with related molecular structures and improved characteristics. Like DCM, all of these chromophores incorporate the dicyanomethylidene [>C═C(CN)$_2$] acceptor group. The synthesis of donor−acceptor analogues of DCM is complicated by the symmetrical nature of the dicyanomethylidenepyran reactant which becomes the acceptor part of the molecule.[8] Reaction of the donor-containing aldehyde with this reactant in a one-to-one stoichiometric ratio tends to produce mixtures in which a considerable portion of the product is the doubly condensed product, requiring difficult chromatographic separation.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1997.

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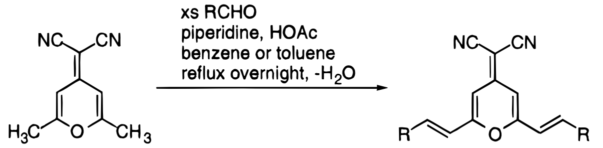


Figure 1. Synthetic scheme for DAD-type analogues.

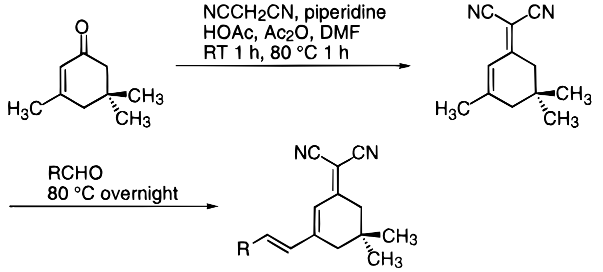


Figure 2. Synthetic scheme for isophorone-type analogues.

We identified two methods to avoid the tedious separation of reaction mixtures related to DCM. The first strategy as depicted in Figure 1 is the use of an excess of donor aldehyde to push the reaction entirely to the doubly condensed product. This produces the donor–acceptor–donor (DAD) series of compounds described previously.[9,10] The DAD compounds are of interest as EO chromophores for both their thermal stability at temperatures over 300 °C and an advantageous nonlinearity–transparency tradeoff. The usual combination of high thermal stability and photobleachability of one of the DAD compounds (DADC) has allowed the use of high processing temperatures in the fabrication of a demonstration Mach–Zender modulator.[11]

To further our studies we wished to also prepare donor–acceptor analogues of DCM. In view of the synthetic difficulties discussed above in obtaining pure monocondensed products, the second strategy we employed was to seek compounds chemically similar to 2,6-dimethyl-4*H*-pyranone as starting materials which could not undergo multiple condensations. Isophorone, verbenone, and chromone are such materials. As shown in Figure 2, isophorone can be condensed with malononitrile to give an intermediate dicyanomethylidene isophorone derivative, and this can be further reacted with a donor-containing aldehyde to produce isophorone-based analogues of type **1**. Alternatively, isophorone, malononitrile, and the donor-containing aldehyde can be condensed in a "one-pot" manner as described by Lemke[12−14] to give the desired NLO chromophore. We have now synthesized a series of compounds of type **1** by employing different donor-containing aldehydes in the synthesis. Table 1 gives their structures. The nonlinear optical properties of **1a** in solution[15] and in poled polymers[16,17] have been investigated by others.

Table 1. Isophorone-Type Analogue Molecular Structures

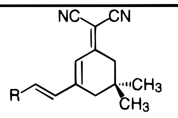
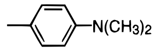
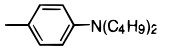
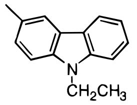
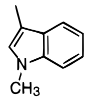
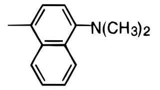
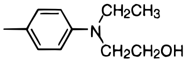
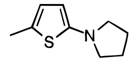
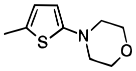
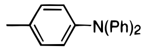
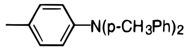
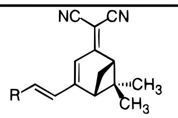
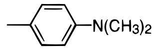
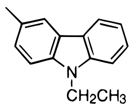
Compound	 R=
1a	
1b	
1c	
1d	
1e	
1f	
1g	
1h	
1i	
1j	

Table 2. Verbenone-Type Analogue Molecular Structures

Compound	 R=
2a	
2b	

Substitution of (1*S*)-(−)-verbenone for isophorone in this synthesis gives chiral analogues of the type **2**. Table 2 shows the structures of the two compounds in this series. For a given donor the physical properties of the type **2** compounds are quite similar to those of type **1**, but their solubilities in polar solvents commonly used to cast polyimide films is markedly improved. A third class of compounds can be made by substituting 2-methylchrom-4-one for isophorone in the synthesis yielding compounds of the type **3** (see Table 3).

Protection of polyene chains in NLO chromophores by means of aliphatic rings was previously proposed by Cabrera and co-workers.[18] The compounds described in that work exhibited appreciable values of β, as anticipated, but no thermal stability information was provided. Accordingly, we have measured both the

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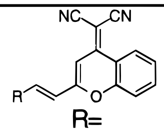
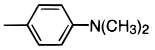
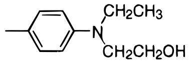
Table 3. Chromone-Type Analogue Molecular Structures

Compound	
3a	
3b	

nonlinearities and thermal decomposition temperatures of the isophorone derivatives in order to determine the extent to which this kind of structure evades the familiar tradeoff between the two. While this paper was in preparation Shu, Jen, and co-workers[19,20] reported the incorporation of isophorone rings into configuration-locked triene nonlinear optical chromophores and showed this to give an enhancement of their thermal stabilities over the corresponding simple triene compounds.

Experimental Section

Synthesis. All organic chemicals were purchased from Aldrich Chemical Co. except as noted and were used as received. Compound **1a** and 3-dicyanomethylidene-1,5,5-trimethylcyclohex-1-ene were synthesized following the procedures of Lemke.[13] The latter compound was also prepared by the condensation of isophorone with malononitrile using ammonium acetate and the azeotropic removal of water.[21] Compounds **1b** and **2a** were reported earlier.[22] Melting points (mp) were determined in capillary tubes on a Mel-Temp II capillary melting point apparatus utilizing a digital thermometer and are uncorrected. Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at room temperature (RT) on a Varian XL-300 NMR spectrometer using deuteriochloroform ($CDCl_3$) as solvent and tetramethylsilane (TMS) as an internal reference unless otherwise indicated. Chemical shifts are reported in parts per million (ppm). Fourier transform infrared (FT-IR) spectra were measured on a KVB/Analect RFX300 FT-IR spectrometer. Ultraviolet−visible (UV−vis) spectra were obtained on a Varian Cary 5E spectrometer. Elemental microanalyses were performed by Desert Analytics (Tucson, AZ).

5-(1-Morpholinyl)-2-thiophenecarboxaldehyde. A mixture of 5-bromo-2-thiophenecarboxaldehyde (23.88 g, 116 mmol), morpholine (11 mL, 126 mmol), anhydrous potassium carbonate (17.68 g, 128 mmol), and Aliquat 336 (0.5 mL) in dimethyl sulfoxide (125 mL) was stirred mechanically under argon at 110 °C for 2 days. After cooling to RT, the reaction mixture was added to water (700 mL). The resulting precipitate was filtered, washed with water, and air-dried. The crude solid was dissolved in 8/2 dichloromethane/ethyl acetate, passed through a short bed of silica gel, and then recrystallized from benzene/hexane to give the product as a reddish brown solid, 16.52 g (72%): mp 127−129 °C (lit.[23] 125−127 °C).

4-Dicyanomethylidene-2-methylchromene. Malononitrile (0.79 g, 12 mmol) and 2-methylchrom-4-one[24] (1.73 g, 10.8 mmol) were refluxed together overnight in acetic anhydride (10 mL). The reaction mixture was cooled to RT and filtered. The crude solid was washed with acetic anhydride, then treated with boiling water (20 mL), and refiltered. Flash chromatography (65/35 dichloromethane/hexane) and recrystallization from ethyl acetate/hexane gave the pure product as pale yellow crystals, 0.80 g (36%): mp 185−186 °C (lit.[25,26] 332−334 °C, 194−196 °C); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 6.72 (s, 1H), 7.42−7.49 (m, 2H), 7.68−7.75 (m, 1H), 8.92 (dd, 1H, $J = 1.4$ and 8.6 Hz); FT-IR (KBr) 2212 and 2200 cm^{-1} (CN stretch). Anal. Calcd for $C_{13}H_8N_2O$: C, 74.99; H, 3.87; N, 13.45. Found: C, 75.03; H, 3.75; N, 13.34.

Compound 1c. A solution of isophorone (8.25 mL, 55 mmol), malononitrile (3.15 mL, 50 mmol), piperidine (0.90 mL, 9.1 mmol), glacial acetic acid (0.20 mL, 3.5 mmol), and acetic anhydride (0.10 g, 1.0 mmol) in *N*,*N*-dimethylformamide (25 mL) was stirred at RT for 1 h and then at 80 °C for 1 h. After adding 9-ethyl-3-carbazolecarboxaldehyde (5.60 g, 25 mmol), the reaction solution was stirred an additional 16 h at 80 °C. Cooling to RT followed by rotoevaporation of the solvent gave a red oil which was redissolved in ethyl acetate. This solution was washed with water, dried with anhydrous sodium sulfate, filtered, and rotoevaporated. Flash chromatography (85/15 hexane/ethyl acetate) and recrystallization from hexane/ethyl acetate gave the product as fine red needles, 1.08 g (11%): mp 195−196 °C; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 6H), 1.46 (t, 3H, $J =$ 7 Hz), 2.50 and 2.56 (two s, 2H each), 4.38 (q, 2H, $J = 7$ Hz), 6.82 (s, 1H), 7.04 (d, 1H, $J = 15$ Hz), 7.25−8.23 (m, 8H); FT-IR (KBr) 2210 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 474 nm ($\epsilon = 2.91 \times 10^4$). Anal. Calcd for $C_{27}H_{25}N_3$: C, 82.83; H, 6.43; N, 10.73. Found: C, 82.50; H, 6.42; N, 10.51.

Compound 1d. Prepared in a manner similar to that for compound **1c** from 1-methylindole-3-carboxaldehyde in 43% yield. Recrystallization from toluene gave the product as a red solid: mp 234.6−235.4 °C; ^{1}H NMR ($CDCl_3$) δ 1.13 (s, 6H), 2.46 and 2.50 (two s, 2H each), 3.83 (s, 3H), 6.73 (s, 1H), 6.97 (d, 1H, $J = 15$ Hz), and 7.24−7.95 (m, 5H); FT-IR (KBr) 2217 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 498 nm ($\epsilon = 3.32 \times 10^4$). Anal. Calcd for $C_{22}H_{21}N_3$: C, 80.70; H, 6.46; N, 12.83. Found: C, 80.88; H, 6.40; N, 12.83.

Compound 1e. Prepared in a manner similar to that for compound **1c** from 4-(dimethylamino)-1-naphthaldehyde in 43% yield. Recrystallization from toluene gave the product as a purple crystalline solid: mp 209−211 °C; ^{1}H NMR ($CDCl_3$) δ 1.12 (s, 6H), 2.57 and 2.60 (two s, 2H each), 2.99 (s, 6H), 6.86 (s, 1H), 7.03 and 7.84 (two d, 1H each, $J = 15$ Hz), 7.06−8.35 (m, 6H); FT-IR (KBr) 2219 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 479 nm ($\epsilon = 2.71 \times 10^4$). Anal. Calcd for $C_{25}H_{25}N_3$: C, 81.71; H, 6.86; N, 11.43. Found: C, 81.64; H, 6.78; N, 11.38.

Compound 1f. Prepared in a manner similar to that for compound **1c** from 4-(ethyl(2-hydroxyethyl)amino)benzaldehyde[27] in 47% yield. Flash chromatography (1/1 ethyl acetate/hexane) and recrystallization from ethyl acetate/hexane gave the product as dark blue-green needles: mp 197.5−198.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 6H), 1.19 (t, 3H, $J = 7.2$ Hz), 2.43 and 2.55 (two s, 2H each), 3.48 (q, 2H, $J = 7.2$ Hz), 3.52 (t, 2H, $J = 5.9$ Hz), 3.82 (t, 2H, $J = 5.9$ Hz), 6.71 and 7.37 (two d, 2H each, $J = 9$ Hz), 6.73 (s, 1H), 6.77 and 6.98 (two d, 1H each, $J = 16$ Hz); FT-IR (KBr) 2215 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 534 nm ($\epsilon = 4.17 \times 10^4$). Anal. Calcd for $C_{23}H_{27}N_3O$: C, 76.42; H, 7.53; N, 11.62. Found: C, 76.69; H, 7.74; N, 11.51.

Compound 1g. A solution of isophorone (0.69 mL, 4.61 mmol), malononitrile (0.28 g, 4.19 mmol), piperidine (2 mL), glacial acetic acid (1 mL), and acetic anhydride (1 mL) in *N*,*N*-dimethylformamide (5 mL) was stirred at RT for 1 h and then 80 °C for 1 h. A solution of 5-(1-pyrrolidinyl)-2-thiophenecarboxaldehyde[28] (0.76 g, 4.19 mmol) in *N*,*N*-dimethylformamide (10 mL) was added, and the reaction solution was stirred at

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80 °C for 2.5 h and then cooled to RT. Water (100 mL) was added, and the reaction mixture was extracted with dichloromethane (3 × 100 mL). The combined organic extracts were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried with anhydrous magnesium sulfate, filtered, and rotoevaporated. The crude material was flash chromatographed (8/2 dichloromethane/hexane) and recrystallized from ethyl acetate/hexane to give the product as shiny blue crystals, 0.35 g (24%): mp >200 °C, sublimes; ^{1}H NMR ($CDCl_3$) δ 1.04 (s, 6H), 2.07−2.11 (m, 4H), 2.38 and 2.53 (two s, 2H each), 3.36−3.41 (m, 4H), 5.75 and 6.98 (two d, 1H each, J = 4.0 Hz), 6.31 and 7.13 (two d, 1H each, J = 15.2 Hz), 6.62 (s, 1H); FT-IR (KBr) 2209 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 618 nm ($\epsilon = 5.75 \times 10^4$). Anal. Calcd for $C_{21}H_{23}N_3S$: C, 72.17; H, 6.63; N, 12.02; S, 9.17. Found: C, 72.12; H, 6.66; N, 12.04; S, 9.24.

Compound 1h. A solution of isophorone (1.02 mL, 6.83 mmol), malononitrile (0.41 g, 6.21 mmol), piperidine (2 mL), glacial acetic acid (1 mL), and acetic anhydride (1 mL) in *N*,*N*-dimethylformamide (5 mL) was stirred at RT for 0.5 h and then at 80 °C for 1 h. After adding 5-(1-morpholinyl)-2-thiophenecarboxaldehyde (1.22 g, 6.21 mmol) the reaction solution was stirred overnight at 80 °C, then cooled to RT, added to water (100 mL), and extracted with dichloromethane (3 × 150 mL). The combined organic extracts were washed with water (1 × 200 mL) and brine (1 × 200 mL), dried with anhydrous magnesium sulfate, filtered, and rotoevaporated. The crude material was flash chromatographed using 97/3 dichloromethane/ethyl acetate as eluent and recrystallized from ethyl acetate/hexane to give the product as shiny blue crystals, 0.78 g (34%): mp >235 °C, sublimes; ^{1}H NMR ($CDCl_3$) δ 1.07 (s, 6H), 2.40 and 2.57 (two s, 2H each), 3.27 and 3.87 (two t, 4H each, J = 4.8 Hz), 6.05 and 6.97 (two d, 1H each, J = 4.0 Hz), 6.42 and 7.11 (two d, 1H each, J = 15.5 Hz), 6.69 (s, 1H); FT-IR (KBr) 2213 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 556 nm ($\epsilon = 4.32 \times 10^4$). Anal. Calcd for $C_{21}H_{23}N_3OS$: C, 69.01; H, 6.34; N, 11.50; S, 8.77. Found: C, 68.67; H, 6.19; N, 11.40; S, 8.61.

Compound 1i. A solution of isophorone (0.97 g, 6.81 mmol), malononitrile (0.42 g, 6.36 mmol), piperidine (2 mL), glacial acetic acid (1 mL), and acetic anhydride (1 mL) in *N*,*N*-dimethylformamide (5 mL) was stirred at RT for 0.5 h and then at 80 °C for 1 h. After adding 4-(diphenylamino)-benzaldehyde (1.74 g, 6.36 mmol, H. W. Sands Corp.) the reaction solution was stirred overnight at 80 °C, cooled to RT, and added to water (150 mL). The resulting precipitate was filtered, washed with water, and redissolved in dichloromethane. The organic solution was dried with anhydrous magnesium sulfate, filtered, and rotoevaporated. Flash chromatography (65/35 dichloromethane/hexane) and recrystallization from ethyl acetate/hexane gave the product as dark red needles, 1.19 g (42%): mp 188−189 °C; ^{1}H NMR ($CDCl_3$) δ 1.09 (s, 6H), 2.47 and 2.61 (two s, 2H each), 6.81 (s, 1H), 6.87 (d, 1H, J = 15.8 Hz), 6.99−7.40 (m, 15H); FT-IR (KBr) 2219 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 496 nm ($\epsilon = 4.03 \times 10^4$). Anal. Calcd for $C_{31}H_{27}N_3$: C, 84.32; H, 6.16; N, 9.52. Found: C, 84.34; H, 6.28; N, 9.51.

Compound 1j. A mixture of 3-dicyanomethylidene-1,5,5-trimethylcyclohex-1-ene (2.43 g, 13 mmol), 4-bis(4-methylphenylamino)benzaldehyde (3.92 g, 13 mmol, Hodogaya Chemical Co. Ltd.), piperidine (1 drop), and toluene (20 mL) was stirred and refluxed for 12 h. The product mixture was cooled to room temperature, and the solid (4.59 g) was collected by suction filtration and washed with a small amount of hexanes. A small second crop (0.72 g) was obtained from the mother liquor. The initial crop was recrystallized from a mixture of methylcyclohexane and toluene, filtered, and dried in vacuo at 75 °C overnight to give the product as greenish-black crystals, 3.73 g (61%). Further purification by flash chromatography (1/1 hexane/dichloromethane) followed by recrystallization from ethyl acetate/hexane gave the analytical sample: mp 216−217 °C; ^{1}H NMR ($CDCl_3$) δ 1.06 (s, 6H), 2.33 (s, 6H), 2.45 (s, 2H), 2.57 (s, 2H), 6.77−7.33 (m, 15H); FT-IR (KBr) 2216 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 510 nm ($\epsilon = 3.99 \times 10^4$). Anal. Calcd for $C_{33}H_{31}N_3$: C, 84.40; H, 6.65; N, 8.95. Found: C, 84.10; H, 6.64; N, 8.93.

Compound 2b. A solution of (1*S*)-(−)-verbenone (8.26 g, 55.0 mmol), malononitrile (3.15 mL, 50 mmol), glacial acetic acid (0.2 mL), acetic anhydride (0.5 mL), and piperidine (0.9 mL) in *N*,*N*-dimethylformamide (25 mL) was stirred at RT for 1 h and then at 80 °C for 1 h. After adding 9-ethyl-3-carbazolecarboxaldehyde (5.60 g, 25 mmol) and stirring for 3.5 h at 80 °C, the reaction solution was cooled to RT, and the solvent was rotoevaporated. The residue was flash chromatographed (4/1 hexane/ethyl acetate) and recrystallized twice from toluene to give the product as a dark orange solid, 1.95 g (19%): mp 197.2−198 °C; ^{1}H NMR ($CDCl_3$) δ 0.94 (s, 3H), 1.45 (t, 3H, J = 7.3 Hz), 1.64 (s, 3H), 1.93 (d, 1H, J = 9.2 Hz), 2.91 (ddt, 1H, J = 9.2, 5.5, and 5.5 Hz), 3.23 (dd, 1H, J = 5.5 and 5.5 Hz), 3.36 (ddd, 1H, J = 5.5, 5.5, and 1.6 Hz), 4.37 (q, 2H, J = 7.3 Hz), 6.66 (s, 1H), 7.03 (d, 1H, J = 15.8 Hz), 7.22−8.26 (m, 8H); FT-IR (KBr) 2217 cm^{-1} (CN stretch); UV−vis (NMP) λ_{max} 477 nm ($\epsilon = 3.09 \times 10^4$). Anal. Calcd for $C_{28}H_{25}N_3$: C, 83.34; H, 6.24; N, 10.41. Found: C, 83.64; H, 6.49; N, 10.24.

Compound 3a. A solution of 4-(dimethylamino)benzaldehyde (0.36 g, 2.4 mmol), 4-dicyanomethylidene-2-methylchromene (0.45 g, 2.2 mmol), piperidine (1 mL), and glacial acetic acid (0.5 mL) in toluene (50 mL) was refluxed overnight under argon using a Dean−Stark trap. The reaction mixture was cooled to RT and filtered. The crude solid was washed with toluene and hexane and then recrystallized from acetonitrile to give the product as dark red needles, 0.47 g (64%): mp 267−269 °C; ^{1}H NMR ($CDCl_3$) δ 3.07 (s, 6H), 6.57 (d, 1H, J = 15.7 Hz), 6.75 (d, 2H, J = 8.6 Hz), 6.77 (s, 1H), 7.37−7.60 (m, 5H), 7.67−7.74 (m, 1H), 8.90 (dd, 1H, J = 1.5 and 8.4 Hz); FT-IR (KBr) 2204 and 2191 cm^{-1} (CN stretch); UV−vis λ_{max} (NMP) 530 nm ($\epsilon = 4.84 \times 10^4$). Anal. Calcd for $C_{22}H_{17}N_3O$: C, 77.86; H, 5.05; N, 12.38. Found: C, 77.75; H, 5.07; N, 12.40.

Compound 3b. A solution of 4-(ethyl(2-hydroxyethyl)-amino)benzaldehyde (0.77 g, 3.98 mmol), 4-dicyanomethylidene-2-methylchromene (0.80 g, 3.84 mmol), piperidine (1 mL), and glacial acetic acid (0.5 mL) in toluene (125 mL) was refluxed overnight under argon using a Dean−Stark trap. The reaction mixture was cooled to RT and filtered. The crude solid was washed with toluene and hexane, then flash chromatographed using ethyl acetate/dichloromethane 1/9 as eluent. The purified material was recrystallized from acetonitrile to give the product as dark blue needles, 1.18 g (80%): mp 210−211.5 °C; ^{1}H NMR ($CDCl_3$) δ 1.24 (t, 3H, J = 6.9 Hz), 3.50−3.60 (m, 4H), 3.87 (br s, 2H), 6.56 (d, 1H, J = 15.5 Hz), 6.75−6.90 (m, 3H), 7.38−7.59 (m, 5H), 7.71 (t, 1H, J = 7.71 Hz), 8.89 (dd, 1H, J = 1.2 and 8.5 Hz); UV−vis λ_{max} (NMP) 544 nm ($\epsilon = 5.17 \times 10^4$); FT-IR (KBr) 2189 and 2204 cm^{-1} (CN stretch). Anal. Calcd for $C_{24}H_{21}N_3O_2$: C, 75.18; H, 5.52; N, 10.96. Found: C, 75.13; H, 5.57; N, 10.86.

EFISH Experimental. Electric field-induced second harmonic (EFISH) generation experiments were performed as previously described[29] in order to determine the quantity $\mu\beta$ at the experimental wavelength of 1907 nm (the Stokes Raman line obtained from the YAG fundamental of 1064 nm in a hydrogen cell). The second harmonic signals from chromophore solutions in chloroform were referenced to a quartz standard[30] ($d_{11} = 6.7 \times 10^{-10}$ esu), and the B convention of Willetts et al.[31] was used. The dielectric constants of the solutions were measured and used to determine dipole moments independently as previously described.[29] The resulting value of β(1907 nm) was extrapolated to zero frequency (β_0) using the two-level model of Oudar and Chemla,[32] and the absorption maximum was determined by UV/visible spectroscopy in chloroform solution. The EO figure of merit[30] for applications at 1300 nm (referred to here as the nonlinearity) was determined by extrapolating β_0 to 1300 nm using the

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Table 4. Analogue Physical Properties[a]

compound	mp	λ_{max}	T_0
1a	226–228	519	286
1b	119–120	539	309
1c	195–196	474	343
1d	234.5–235.5	498	326
1e	209–211	479	334
1f	187.5–188.5	534	317
1g	>200[b]	618	
1h	>235[b]	556	328
1i	188–189	496	346
1j	216–217	510	344
2a	193–194	525	289
2b	197.2–198	477	389
3a	267–269	530	361
3b	210–211.5	544	370

[a] Melting points (mp) and onset temperatures of weight loss (T_0) in N_2 are given in °C, wavelengths are given in nm, and *N*-methylpyrrolidinone (NMP) was used as the solvent for the λ_{max} measurements. [b] Sublimes.

Table 5. EFISH Experimental Data for Isophorone-Type Analogues[a]

compound	λ_{max}	f	μ	β	β_0	$\mu\beta_0$/MW	$\mu\beta_{1300}$/MW	T_d
1a	508	0.83	8.7	246	164	4.50	5.94	307
1b	530	0.84	9.1	277	177	4.02	5.45	268
1c	464	0.62	8.3	146	105	2.22	2.79	322
1d	482	0.74	9.0	114	79	2.17	2.78	317
1e	478	0.68	6.8	146	103	1.91	2.43	315
1f	506	0.78	8.4	219	146	3.39	4.68	306
1h	530	0.80	7.8	213	136	2.91	3.95	290
1i	502	0.63	7.1	242	163	2.61	3.42	313
1j	520	0.74	7.3	352	229	3.56	4.75	367

[a] Wavelengths are given nm, dipole moments in debye, hyperpolarizabilities in units of 10^{-30} esu, and temperatures in °C. All spectral and EFISH data were taken in chloroform solution.

dispersion relationship for the Pockels effect under the two-level model, multiplying by the dipole moment, and dividing by the molecular weight (MW).

Results

Physical Properties of Isophorone-Type Analogues. Table 4 gives the melting point (mp), absorption maximum (λ_{max}), and thermal weight loss temperature (T_0) as determined by thermogravimetric analysis (TGA) in nitrogen for each of the analogues synthesized. The compounds exhibit intense absorption maxima in the wavelength range 470–545 nm when measured in *N*-methylpyrrolidinone (NMP).

EFISH Results. Table 5 lists the spectral properties (λ_{max} and oscillator strength, f), dipole moments, nonlinear optical properties (β and β_0), EO figures of merit, and thermal decomposition temperatures (T_d) for each of the isophorone derivatives. Calculations of β_0 were made using the two-level model. Decomposition temperatures were measured by differential scanning calorimetry in air, scanning at 20 °C/min. Extrapolation of the exotherm onset back to the baseline yielded T_d.

Nonlinearity–Transparency Relationship. Thienyl-based chromophores may be made by substituting a thiophenecarboxaldehyde for the benzaldehyde reactant in the Lemke synthesis. These compounds are generally lower in thermal stability than the corresponding phenyl-containing compounds and have red-shifted absorption maxima. While **1g** was not soluble enough in chloroform to permit inclusion in the EFISH study, the dipole moment μ and quadratic hyperpolarizability β of the morpholino analogue **1h** were determined to be 7.8 D and 213 × 10^{-30} esu, respectively. Calculation of β_0 using the two-level model as described above gave a value of 136 × 10^{-30} esu, which is not significantly greater than β_0 values for the phenyl-containing compounds. The λ_{max} of **1h** in NMP appears at 556 nm as compared with the peaks at 474 and 519 nm for DCM and **1a**, respectively. We hesitate to draw conclusions on such limited data; however, we can state that at this time we do not see a significant increase in nonlinearity upon thienyl substitution for these compounds.

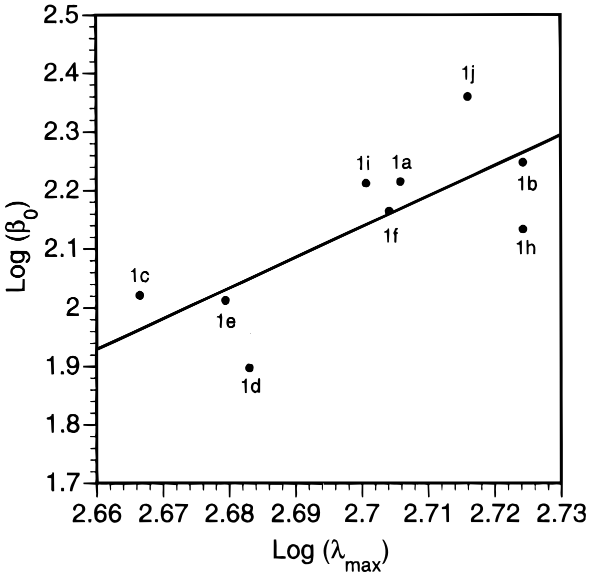

Figure 3. log(λ_{max}) versus log(β_0) plot for isophorone-type analogues.

We have more generally examined the tradeoff between nonlinearity and transparency by plotting log β_0 vs log λ_{max}, fitting a straight line to the plot and determining the slope of the best fit line (see Figure 3). This technique allows us to compare the nonlinearity/transparency tradeoff with that observed for other classes of chromophores which have been similarly analyzed.[33]

Thermal Stability. Relative thermal stability was determined using thermogravimetric analysis (TGA) under nitrogen atmosphere at a heating rate of 20 °C/min. The results obtained for a selected few of the analogues are shown in Figure 4. Weight loss in this experiment may be due to either sublimation or decomposition of the chromophore. As can be seen, **1a** and **2a** lose weight at slightly lower temperatures than does DCM. Higher weight loss temperatures are seen in the compounds in which either the nitrogen donor group (**1c** and **1d**) or the dicyanomethylidene acceptor group (**3a**) is part of a fused ring system. The compound which survives to highest temperature is **1c**, in which the donor amino group is part of a carbazole ring system. This is consistent with our results for the DAD series, in which the carbazole-containing compound DADC loses less than 2% of its weight when heated to 400 °C at a rate of 20 °C/min.

Discussion

It has been noted previously[30] that chromophores with nonlinearities ($\mu\beta_{1300}$/MW) above 3.0 and thermal de-

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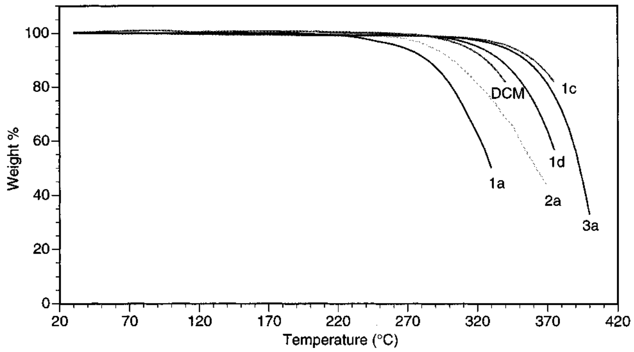

Figure 4. Plot of thermogravimetric analysis results for selected analogues in a N_2 atmosphere with a heating rate of 20 °C/min.

Table 6. Isophorone-Type Analogue Excited-State Dipole Moments[a]

compound	excited-state μ (D)	compound	excited-state μ (D)
1a	18.0	**1f**	17.3
1b	17.9	**1h**	14.9
1c	18.8	**1i**	19.7
1d	14.9	**1j**	20.9
1e	15.4		

[a] Excited-state dipole moments were determined from EFISH and spectral data as described in refs 2 and 38.

composition temperatures above 300 °C are quite rare. The most striking aspect of the data in Table 5 is that six of the nine compounds meet the nonlinearity criterion, seven meet the thermal stability criterion, and four meet both. Partial protection of the triene bridge with the isophorone ring has afforded a surprising amount of thermal stability, while allowing the β values to remain substantial. The oscillator strengths also remain high (0.74 on average) as do the dipole moments (8 D). Given the oscillator strength, the absorption maximum, and β_0, it has been shown[2] that the change in dipole moment upon excitation can be calculated, under the assumptions of the two-level model. Even though the ground-state dipole moments of these compounds are appreciable, the excited-state dipole moments range from 15 to 21 D, as shown in Table 6.

The degree to which a series of similar compounds suffers from the tradeoff between nonlinearity and transparency is typically quantified by determining the slope of a log−log plot of β vs λ_{max}. Most classes of compounds examined to date have exhibited slopes of approximately 6 (6.5 ± 1.4 for triphenylimidazoles,[29] 6.0 ± 0.7 and 7.1 ± 1.1 for tolanes,[34,35] 6.5 ± 1.0 for pyrazoles,[36] 6.2 ± 0.7 for thiazoles,[37] and 6.1 ± 0.7 for coumarins[38]). Such a plot for the isophorone series is shown in Figure 3. The slope of this plot is 5.2 ± 1.7, equal to the typical value within experimental error. Therefore, the improved thermal stability in these compounds has not led to any decrease in transparency (at least as measured by λ_{max}) for a given nonlinearity.

Conclusions

A series of nonlinear optical chromophores with dicyanomethylidene acceptor groups has been synthesized and characterized. Nine of these compounds include an isophorone cyclohexene ring as part of the delocalized bridge segment. Not only are the dipole moments and hyperpolarizabilities encouragingly large, but their thermal decomposition temperatures are substantially higher than one would expect from unsubstituted trienes. The synthesis of these isophorone derivatives is facile compared to that of the previously studied dicyanomethylidenepyran series, because the asymmetric structure of the parent isophorone allows only one condensation reaction rather than two, thus obviating the need for a difficult chromatographic separation. The increase in hyperpolarizability with absorption maximum is the same as for most other classes of chromophores. It has recently been shown[39] that compounds of this type form glasses that can be used for holographic optical storage, suggesting that materials of very high chromophore concentration and good optical quality can be prepared.

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