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Non-linear absorption of 2,5-dialkynyl thiophenes

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ABSTRACT: Three diarylalkynyl-substituted thiophenes were synthesized and the optical power limiting (OPL) effect at 532 nm was investigated for solutions of these compounds. The relationship between the OPL and parameters obtained from molecular-orbital-based calculations is discussed. Semi-empirical calculations indicate that the compounds can have a broad distribution of conformations due to inter-ring twisting, but that the second hyperpolarizability (γ) can be significant despite a ring twist. The calculations imply that substitution by alkyl groups can lead to enhanced γ values. The measurements and calculations show a greater increase of the OPL and γ effects from compound **5** to **6** than from **6** to **7**. For these compounds, which differ mainly by the length of the π-electron system, the magnitude of non-linear absorption seems to be well correlated with several properties of the electronic ground state estimated by standard *ab initio* molecular orbital calculations, as well as with γ values from the semi-empirical calculations. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: optical limiting; non-linear absorption; hyperpolarizability; thiophenes; thiophenyl; phenylacetylenes

INTRODUCTION

Over the last few decades there has been a considerable optimism concerning the use of non-linear optical (NLO) organic materials for all-optical switching and optical computing.[1–5] Both a light-induced refractive index change as well as a transmittance change of a material should be useful for all-optical signal manipulation. The non-linear refraction of a bulk substance has its equivalence at the molecular level in the real part of the second hyperpolarizability tensor γ.[6,7] Within the same theoretical framework, the imaginary part of γ describes non-linear absorption, of which two-photon absorption (TPA) is an important mechanism.[6] The TPA event is being applied already in two-photon fluorescence microscopy[8,9] and is promising for other applications such as data storage[10] and optical power limiting (OPL).[11–17] Another mechanism that can contribute to the OPL performance of a material is excited state absorption (ESA), where one or several excited states (singlets and/or triplets) reveal a stronger absorption of light than that of the electronic ground state.[12–15,18,19]

This work focuses on the optical limiting behavior of dialkynyl-substituted thiophenes **5**–**7** (Scheme 1) at the wavelength of 532 nm in tetrahydrofuran solution. Earlier investigations on π-conjugated molecules have shown that the third-order optical non-linearity can be increased by incorporation of a sulfur atom in the organic structure.[20] The increased non-linearity was seen as the result of strong π-overlap and involvement of the sulfur atom orbitals in the molecular π-orbitals.

In comparison with benzenoid rings, the heterocyclic rings in the series furan, thiophene and selenophene are less aromatic and can have stronger interaction with attached groups. By the same token, the thiophene ring is a slightly better π-electron donor in comparison with the benzene ring. The ability of thiophenes to take part in electron delocalization while still showing only weak absorption of visible light is one reason for our choice of thiophenes for this study. A fair number of compounds having a thiophenyl group have been studied with respect to third-order NLO effects,[21] and a few will be mentioned briefly here. Experimental[22] and theoretical[23,24] investigations have shown that thiophene displays significant instantaneous second hyperpolarizability, i.e. a purely electronic process, must likely originating from localized electrons on the sulfur atom. It has been shown also that thiophenes with unsaturated substituents in the 2,5-positions can display TPA, e.g. 2,5-*bis*-(benzothiazol-2-yl)-3,4-(dimethoxy)-thiophene at ~602 nm.[25,26] Significant values of $\chi^{(3)}$ and the two-photon absorption coefficient (β) of dithienylethylenes have been found by degenerate four-wave mixing (DFWM) experiments with laser pulses in the picosecond regime at 532 nm and by OPL experiments in the visible region, respectively.[27]

Copolymers of ethynyl-bridged carbazole and thiophene units, being virtually transparent above 475 nm,

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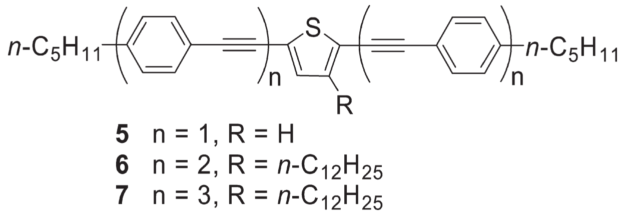


Scheme 1

have been studied using picosecond pulses at 1064 nm with the DFWM technique.[28] Large optical non-linearities, originating from instantaneous electronic polarization, were determined for both a solution and a thin film of the polymer. Interestingly, investigations on thiophene and bithiophene using 400 nm sub-picosecond or femtosecond pulses have shown ultrafast triplet state formation from a TPA-populated singlet state for the compounds.[19,29] At least bithiophene was found to have excited singlet and triplet state absorption. In another study, triplet thiophene was probed by weak phosphorescence, with a maximum at 430 nm.[30] Hence, we found the thiophene building block to be interesting in the search for efficient OPL compounds because both TPA and ESA may take place in thiophene derivatives.

EXPERIMENTAL

General

Infrared measurements were performed with a Mattson Fourier-transform 60AR instrument. The transmission spectra were recorded with Shimadzu UV-3101PC and Cary 5G UV-VIS-NIR spectrophotometers. The former was used also for optical absorbance measurements. The ^{1}H and ^{13}C NMR spectra were obtained on a Bruker DRX-400 instrument. Tetramethylsilane (TMS) was used as an internal chemical shift standard for all CDCl$_3$ samples except for the ^{13}C NMR spectrum of compound **7**, where the tetrahydrofuran-d_8 ([^{2}H$_8$]THF) ^{13}C—O peak at δ 67.15 was used as a reference. Mass spectrometry for different compounds was carried out on either of two instruments: a JMS-SX/SX102A double-focusing magnetic sector mass spectrometer (Jeol, Tokyo), using direct inlet and electron impact ionization (EI+), with ionizing voltage 70 eV, acceleration voltage 10 kV and resolution 1000; or a Waters Micromass ZQ quadrupole mass spectrometer for compounds **6** and **7**, using direct inlet, electrospray ionization (ESI) and a sampling cone voltage of 40 V. The CH$_3$OH–CH$_2$Cl$_2$ (1:2) solutions were 0.1 mM with respect to both the thiophene and AgNO$_3$.[31] An *f*/5 optical arrangement and a frequency-doubled Nd:YAG laser delivering 5 ns pulses at 532 nm with a repetition rate of 10 Hz was used in the OPL investigations. The detailed set-up has been reported elsewhere.[32,33] The OPL measurements were performed on tetrahydrofuran (THF) solutions of compounds **5**–**7** in 2 mm quartz cuvets. The focus of the laser beam was positioned carefully at the center of the cell to avoid damage of quartz surfaces and chemical reactions of the compounds at the surfaces. The OPL of neat THF in a quartz cuvet was found to be insignificant compared with that of solutions of the investigated compounds.

Quantum chemistry calculations

Semi-empirical AM1[34] calculations of non-resonant (static) γ were performed with MOPAC 2000[35] using a time-dependent Hartree–Fock (TDHF) method.[36] ZINDO calculations[37,38] were carried out with the Gaussian 98W[39] package and AM1-optimized geometries. Molecular geometry optimizations were also performed with the B3LYP[40] quantum chemistry method and the 6–31G(d)[41] basis set, using Gaussian 98W software.

Synthesis

The compounds 4-pentylphenylacetylene, 2,5-diiodothiophene, 3-*n*-dodecyl-2,5-dibromothiophene and PdCl$_2$(PPh$_3$)$_2$ were obtained from Aldrich and were used as received. The solvents used in the reactions were of p.a. quality. 4-(4-Iodophenyl)-2-methyl-3-butyn-2-ol was prepared as described earlier.[42,43] Thin-layer chromatography (TLC) was performed on silica gel 60 F$_{254}$ (Merck) and flash column chromatography was performed on silia gel (Matrex 60 Å, 35–70 μm, Grace Amicon).

2-Methyl-4-[4-(4-pentylphenylethynyl)phenyl]-3-butyn-2-ol (1). To a solution of 4-(4-iodophenyl)-2-methyl-3-butyn-2-ol (4.1 g, 14 mmol) in 80 ml of pyridine and 80 ml of triethylamine was added PdCl$_2$(PPh$_3$)$_2$ (20 mg, 0.29 mmol), PPh$_3$ (60 mg, 0.11 mmol) and CuI (55 mg, 0.29 mmol). 4-Pentylphenylacetylene (4.8 g, 28 mmol) was added dropwise to the mixture and the reaction was stirred for 20 h at room temperature. The solvent was removed under reduced pressure and the resultant pale brown solid was collected using ether. The organic phase was washed twice with 50 ml of 1 M HCl, twice with 50 ml of water and dried with MgSO$_4$. Recrystallization from heptane of the brownish solid gave 4.1 g (89%) of white fluffy product. $R_f = 0.25$ in heptane–EtOAc (10:1); m.p. = 99–102 °C. IR: ν(cm^{-1}) = 3471 br m, 2925 s, 2854 m, 2163 w, 1516 s, 1452 m, 1360 s, 1271 m, 1157 s; ^{1}H NMR (CDCl$_3$): $\delta = 0.87$ (t, 3H), 1.29 (m, 4H), 1.60 (m, 8H), 2.00 (s, 1H), 2.59 (t, 2H), 7.15 (d, 2H), 7.37 (d, 2H), 7.42 (t, 4H); ^{13}C NMR (CDCl$_3$): $\delta = 14.0$, 22.5, 30.9, 31.4, 35.9, 65.6, 81.9, 88.3, 91.4, 95.4, 120.1, 122.3, 128.5, 131.4, 131.5, 131.6, 143.7.

1-Ethynyl-4-(4-pentylphenylethynyl)benzene (2). The protected alkyne **1** (1.39 g, 4.2 mmol) was dissolved in 100 ml of benzene, NaH (0.5 g, 50% dispersion in oil) was added and the mixture was slowly distilled until 50 ml of the distillate had been collected. After being allowed to cool, the solution was poured into cold water. The organic phase was dried with $MgSO_4$, filtered and evaporated. The brown–yellow product was passed through a silica column (hexane–EtOAc, 10:1). The resultant yellow product was passed through a short alumina column using hexane as eluent. This gave 1.0 g (88%) of white product. $R_f = 0.9$ in heptane–EtOAc (10:1); m.p. = 65–67 °C. IR: $\nu(\mathrm{cm}^{-1}) = 3270$ s, 2923 s, 2213 w, 1598 w, 1514 m, 1464 m; ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, 3H), 1.30 (m, 4H), 1.59 (m, 2H), 2.59 (t, 2H), 3.15 (s, 1H), 7.16 (d, 2H), 7.40–7.44 (m, 6H); ^{13}C NMR ($CDCl_3$): $\delta = 13.8$, 22.3, 30.7, 31.2, 35.7, 78.5, 83.1, 88.0, 91.4, 119.8, 121.4, 123.8, 128.3, 131.2, 131.3, 131.8, 143.6; EI + MS: *m/z* (int %) = 215 (100), 272 (67).

2-Methyl-4-{4-[4-(4-pentylphenylethynyl)phenylethynyl]phenyl}-3-butyn-2-ol (3). The coupling between compound **2** (0.60 g, 2.2 mmol) and 4-(4-iodophenyl)-2-methyl-3-butyn-2-ol (0.40 g, 1.4 mmol) was performed as described for the synthesis of compound **1**. The yield of compound **3** was 0.50 g (83%); m.p. = 218–220 °C. IR: $\nu(\mathrm{cm}^{-1}) = 3465$ br m, 2925 s, 2856 m, 1924 w, 1518 s, 1454 s, 1373 m, 1270 m, 1157 s; ^{1}H NMR ($CDCl_3$): $\delta = 0.83$ (t, 3H), 1.26 (m, 4H), 1.56 (m, 8H), 1.94 (s, 1H), 2.55 (t, 2H), 7.09 (d, 2H), 7.31–7.42 (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 14.0$, 22.5, 30.9, 31.4, 35.8, 64.5, 81.8, 88.4, 90.7, 91.7, 95.4, 95.6, 120.0, 122.5, 122.7, 122.9, 123.6, 128.5, 131.4, 131.5, 131.6, 132.4, 143.7.

1-Ethynyl-4-(4-(4-pentylphenylethynyl)phenylethynyl)benzene (4). The same procedure as described for synthesis of alkyne **2** from compound **1** was applied for the preparation of compound **4** from compound **3**. The yield of compound **4** was 89%; m.p. = 176–181 °C. IR: $\nu(\mathrm{cm}^{-1}) = 3268$ s, 2915 s, 1926 m, 1517 s, 1407 m, 1267 m; ^{1}H NMR ($CDCl_3$): $\delta = 0.87$ (t, 3H), 1.30 (m, 4H), 1.60 (m, 2H), 2.59 (t, 2H), 3.16 (s, 1H), 7.16 (d, 2H), 7.41–7.48 (m, 10H); ^{13}C NMR ($CDCl_3$): $\delta = 14.0$, 22.5, 30.9, 31.4, 35.9, 79.0, 83.2, 88.4, 90.5, 91.1, 91.7, 120.0, 122.0, 122.4, 123.5, 123.6, 128.5, 131.5, 131.5, 131.5, 132.1, 132.4, 143.7; EI + MS: *m/z* (int %) = 315 (82), 372 (100).

2,5-Di-(4-pentylphenylethynyl)thiophene (5). 2,5-Diiodothiophene (1.5 g, 4.5 mmol) was dissolved in a mixture of 20 ml of pyridine and 20 ml of triethylamine under Ar atmosphere. $PdCl_2(PPh_3)_2$ (60 mg, 0.085 mmol), PPh_3 (70 mg, 0.27 mmol) and CuI (25 mg, 0.13 mmol) were added to the solution, followed by dropwise addition of 4-pentylphenylacetylene (2 g, 12 mmol). The reaction was stirred for 48 h at room temperature. The solvent was removed and the residue dissolved in CH_2Cl_2 and washed with 1 M HCl and water. The organic phase was dried with $MgSO_4$, filtered and evaporated, and the product was purified on a silica column using heptane as eluent. This gave 0.78 g (41%) of a pinkish product; m.p. 62–64 °C. IR: $\nu(\mathrm{cm}^{-1}) =$ 3033 w, 2919 m, 2194 w, 1747 m, 1649 s, 1479 s, 1203 m; ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, 6H), 1.32 (m, 8H), 1.62 (m, 4H), 2.61 (t, 4H), 7.12 (s, 2H), 7.15 (d, 4H), 7.42 (d, 4H); ^{13}C NMR ($CDCl_3$): $\delta = 14.0$, 22.5, 30.8, 31.6, 35.9, 81.7, 94.2, 119.7, 124.7, 128.5, 131.4, 131.5, 143.9; EI + MS: *m/z* (int %) = 424 (100).

3-Dodecyl-2,5-di-[4-(4-pentylphenylethynyl)-phenylethynyl]thiophene (6). To a solution of 3-*n*-dodecyl-2,5-dibromothiophene (0.38 g, 0.9 mmol) in 10 ml of pyridine and 10 ml of triethylamine under Ar atmosphere was added $PdCl_2(PPh_3)_2$ (50 mg, 0.074 mmol), PPh_3 (40 mg, 0.15 mmol) and CuI (20 mg, 0.11 mmol). Alkyne **2** was dissolved in 20 ml of pyridine and added dropwise over a period of 2 h. The solution was stirred for 48 h at room temperature and for 2 h at 50 °C. The solvent was removed and the residue dissolved in CH_2Cl_2 and washed with 1 M HCl and water. The organic phase was dried with $MgSO_4$, filtered and evaporated. The solid was dissolved in hot EtOAc–hexane (5:95) and filtered through a short silica column ($R_f = 0.25$ in hexane). Repeated recrystallization from hot hexane yielded 0.33 g (46%) of compound **6** as yellow crystals; m.p. = 83–85 °C. IR: $\nu(\mathrm{cm}^{-1}) = 3029$ w, 2918 s, 2852 s, 2192 w, 1916 w, 1511 m, 1454 m, 1375 m, 1307 w; ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (m, 9H), 1.25–1.33 (m, 26H), 1.61 (m, 6H), 2.61 (t, 4H), 2.72 (t, 2H), 7.06, (s, 1H), 7.15 (d, 4H), 7.43–7.50 (m, 12H); ^{13}C NMR ($CDCl_3$): $\delta = 14.0$, 14.1, 22.5, 22.7, 29.2, 29.4, 29.4, 29.5, 29.6, 29.7, 29.7, 30.1, 30.9, 31.5, 31.9, 35.9, 83.8, 84.5, 88.5, 88.5, 91.8, 91.9, 93.8, 96.2, 120.0, 120.0, 120.1, 122.2, 122.5, 123.1, 123.5, 123.7, 128.5, 131.2, 131.3, 131.5, 131.5, 133.2, 143.8, 148.1; ESI + MS: $m/z = 899$ ($[\mathbf{6} + \mathrm{Ag}]^+$; significant peaks at 899, 900, 901, 902, as expected from the calculated major isotope distribution at 899.4, 900.4, 901.4, 902.4), 1692 ($[\mathbf{6} + \mathbf{6} + \mathrm{Ag}]^+$; significant peaks at 1692, 1693, 1694, 1695, 1696, as expected from the calculated major isotope distribution at 1691.9, 1692.9, 1693.9, 1694.9, 1695.9).

3-Dodecyl-2,5-di-{4-[4-(4-pentylphenylethynyl)-phenylethynyl]phenylethynyl}thiophene (7). To a solution of 3-*n*-dodecyl-2,5-dibromothiophene (0.11 g, 0.27 mmol) in 5 ml of toluene and 5 ml of triethylamine under Ar atmosphere was added $PdCl_2(PPh_3)_2$ (15 mg, 0.022 mmol), PPh_3 (14 mg, 0.054 mmol) and CuI (6 mg, 0.032 mmol). Alkyne **4** was dissolved in warm toluene and added dropwise over a period of 2 h. After reaction at 90 °C for 48 h, the solvent was removed and the residue dissolved in CH_2Cl_2 and washed with 1 M HCl and water. The organic phase was dried with $MgSO_4$, filtered and evaporated. The solid was dissolved in hot toluene–heptane (50:50) and filtered through a short silica column using heptane–EtOAc (50:50) as eluent ($R_f = 0.4$; heptane–EtOAc, 10:1). The volume of the filtrate was reduced and a yellow precipitate was collected. The solid was recrystallized by dissolving it in hot CH_2Cl_2 and adding hexane until a precipitate was formed. The yield of the yellow product was 75 mg (28%); m.p. = 175–178 °C. IR: $\nu(\mathrm{cm}^{-1}) = 3037$ w, 2921 s, 2851 s, 2188 w, 1922 w, 1517 s, 1454 m, 1407 m, 1307 w; ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (m, 9H), 1.25–1.33 (m, 26H), 1.63 (m, 6H), 2.62 (t, 4H), 2.73 (t, 2H), 7.08 (s, 1H), 7.15 (d, 4H), 7.43–7.50 (m, 20H). ^{13}C NMR (THF-d_8): $\delta = 14.1$, 14.2, 23.1, 23.3, 29.8, 29.9, 30.0, 30.1, 30.3–30.4, 30.7, 31.6, 32.1, 32.6, 36.4, 78.6, 79.0, 79.3, 84.2, 84.8, 88.8, 91.2, 91.2, 91.7, 92.2, 94.2, 96.8, 120.6, 120.9, 123.3, 123.5, 123.8, 124.0, 124.1, 124.5, 129.1, 131.9, 132.0–132.2, 134.1, 144.3, 149.0; ESI + MS: $m/z = 1099$ ($[\mathbf{7} + \mathrm{Ag}]^+$; significant peaks at 1099, 1100, 1101, 1102, 1103, as expected from the calculated major isotope distribution at 1099.4, 1100.4, 1101.4, 1102.4, 1103.4).

RESULTS AND DISCUSSION

Synthesis

A general Pd- and Cu-catalyzed reaction was employed repeatedly to achieve coupling between a haloaryl and an ethynylaryl unit in the preparation of compounds **5**–**7** (Scheme 2).[44] The synthesis of the alkynes also involved protection–deprotection of one terminal alkyne.[42,43] It may be worth mentioning that the coupling with the 2,5-diiodothiophene in the preparation of compound **5** did not result in a better yield than the reaction with a corresponding dibromothiophene for the synthesis of compound **6**. Hence, it appears that more available dibromo thiophenes instead of diiodo analogs can be used for the preparation of larger quantities of this type of compound. The coupling reaction is a convenient and reliable method to build and lengthen arylalkynyl systems, but is likely to result in low overall yields in linear syntheses of extended systems.

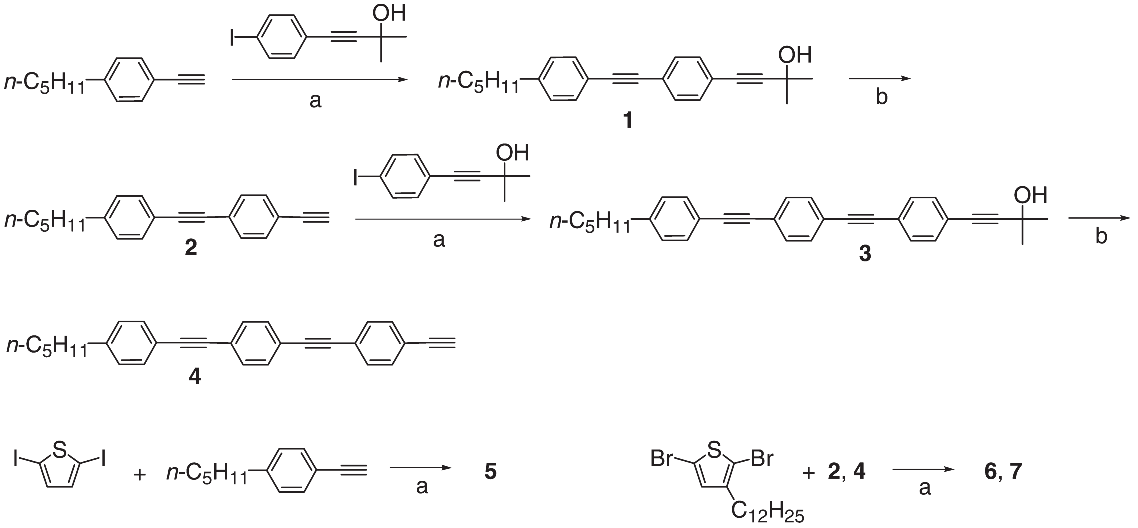
Early work in this project showed that the parent compound of **6** lacking alkyl groups, here denoted **6′**, has rather low solubility in THF. Therefore, the continued work utilized pentyl groups for compound **5** and both pentyl and dodecyl groups for compounds **6** and **7** to increase their solubility. In spite of the alkyl groups, compound **6** and especially compound **7** still have quite low solubility in THF. Even though the unsubstituted compounds were not studied experimentally, the structures **5′**–**7′** were included in the theoretical work reported below.

Structural considerations, calculated properties and absorption spectroscopy of OPL compounds

In this section we wish to give a background for the choice of compounds in the study and report on some structural features and properties of the compounds as derived from quantum chemistry calculations. Some of our guiding points in the search for efficient OPL systems were as follows:

(i) The OPL compounds should be assembled from not more than a few smaller OPL-active molecular entities (A), having significant non-linear absorption in relation to their number of atoms and π electrons. The assembled compounds should, of course, have substantially better OPL capacity than that expected from adding together the OPL response of the subunits.

(ii) The A groups should be connected by bridging groups (B) that allow only a weak electronic



Scheme 2. Reagents and solvents: (a) $PdCl_2(PPh_3)_2$, CuI, PPh_3, pyridine, triethylamine; (b) NaH, C_6H_6

interaction between adjacent A groups and only a moderately efficient interaction between A and B, so that for instance the absorption spectrum of the molecule resembles a superimposition of the spectra of different A and B groups.

(iii) The OPL compounds should have good transparency in the visible range.

(iv) The OPL compounds should be rigid to avoid having the OPL response being averaged by molecular conformations of unknown distribution, which would complicate interpretation of the results. A high molecular symmetry (inversion centre or C_{2v} symmetry) should be an advantage[45] because it may facilitate a theoretical description of various excited states.

(v) The compounds should be stable both chemically and thermally.

Reasons for considering the thiophenyl group as an A component were mentioned in the Introduction. The ethynyl group appeared to be a suitable B component, because its interaction with aromatic rings such as phenyl and thiophenyl can be described as a weak coupling due to π-orbital mismatch. The mismatch arises from a low-lying HOMO and a high-lying LUMO in the ethynyl group. An example of this rather weak interaction is that several *para*-disubstituted diphenylacetylenes (tolanes) show a blue-shift of $\lambda_{\max}$ in the absorption spectrum compared with the corresponding ethylenes (stilbenes).[46] A possible drawback of using ethynyl instead of ethenyl groups may be that somewhat lower γ values can be expected. Such an outcome was demonstrated by THG experiments using 636 nm output wavelength on the tolanes and stilbenes.[46] Nevertheless, a DFWM study at 620 nm on thin films of phenyl-ethynyl compounds having alkoxy substituents showed a $\chi^{(3)}$ value of a phenyl—C≡C—(*p*-phenylene)—C≡C—phenyl compound that was only 46% lower than that of the corresponding polymer,[47] suggesting that rather small units may have significant NLO properties if electron-donating groups are attached to the aromatic rings. Hence the C≡C bridge can, to some extent, in comparison with the C=C spacer, reduce the electronic coupling between π-electron systems and thus provide compounds with low absorbance in the visible region. Obviously, ethynyl *vs.* ethenyl spacers will result in stiffer and more rod-like compounds.

We used phenylene rings to extend the π-system from compound **5** to **6** and **7** in order to investigate the effect of the conjugation length on OPL. In addition to the contribution of π-electrons, the use of phenylene rings is mainly due to synthetic convenience and thermal stability reasons.

Semi-empirical AM1 molecular orbital calculations showed the lowest energy conformations of compounds **5**–**7** to have coplanar rings, as expected. This was also the result from B3LYP/6–31G(d) calculations of compounds **5′**–**7′** (lacking alkyl groups). ZINDO calculations of compound **5** and of somewhat simplified structures of **6** and **7** having methyl instead of the pentyl and dodecyl groups suggested that the compounds should give transparent solutions because the only absorptions near the visible region would be at a shorter wavelength than 400 nm (Table 1). This was corroborated from the UV–VIS absorption spectra of THF solutions of **5**–**7** (Fig. 1). The position of the absorption peak is, as expected, shifted towards the red from compound **5** to **6** and **7**, with absorption maxima of 352, ~380 and 385 nm, respectively. Along with the shift in peak position there is a marked increase in extinction coefficient demonstrating increased oscillator strength for the more conjugated structures. However, although the absorptions increase the yellowish appearance of compounds **6** and **7** compared with **5**, there is virtually no absorption at wavelengths longer than 450 nm. Solutions of all three compounds therefore have good transparency at the highest possible concentrations in THF (see below).

Table 1. Experimental and calculated absorption parameters and γ values of thiophenes **5**–**7** and model thiophenes **5′**–**7′**

	Theoretical			Experimental[a]	
Compound	λ (nm)[b]	f[b]	$\gamma/10^5$[c] (a.u.)	$\lambda_{\max}$ (nm)	$\varepsilon(\lambda_{\max})/10^4$ ($\text{cm}^{-1}\,\text{M}^{-1}$)
5	381	1.60	6.0	352	3.5
6[d]	389	2.95	18.8	380	8
7[d]	393	3.79	35.5	385	13
5′	378	1.50	4.3		
6′	388	3.01	18.0		
7′	392	3.91	35.1		
BMT[e]			2.1		

[a] Tetrahydrofuran solution.

[b] Both λ and f (oscillator strength) for the dominant excitation from ZINDO calculations.

[c] Orientationally averaged second hyperpolarizability from AM1 calculations.

[d] Methyl instead of longer alkyl groups in compounds **6** and **7** were used to simplify the calculations.

[e] 2,5-*Bis*(benzothiazol-2-yl)-3,4-(dimethoxy)thiophene; see text.

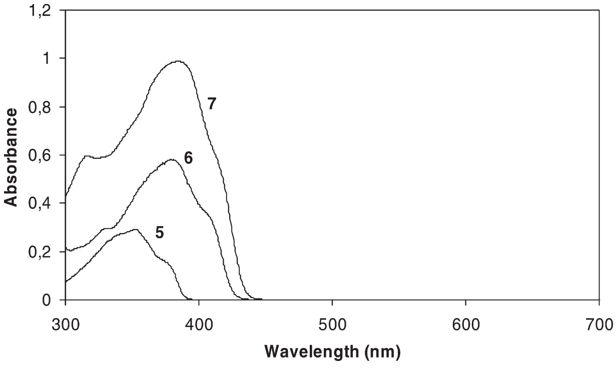


Figure 1. Absorption spectra for thiophenes **5**–**7** in THF

The hyperpolarizability calculations show substantial increase of non-resonant γ from the smaller to the larger compounds: almost by a factor of six from compound **5** to **7** and a factor of eight from **5′** to **7′** (Table 1). The γ values increase more when going from **5′** to **6′** than from **6′** to **7′**. This is also found for the series of compounds **5**–**7** but here the trend is less pronounced. In addition, the calculations show that alkyl substitution gives an increase of γ; this is especially apparent when **5** is compared with **5′**. Because alkyl groups function as weak electron donors in normal organic molecules, other electron-donating substituents can be of interest for modification of the OPL effect in this type of compound.

For a comparison with compounds **5**–**7**, γ of the related compound 2,5-*bis*(benzothiazol-2-yl)-3,4-(dimethoxy) thiophene (see Introduction) was calculated. This compound, abbreviated to BMT in Table 1, has a markedly lower γ value than the other structures, which suggests that compounds **5**–**7** can be better choices for OPL studies than BMT. However, one should bear in mind that calculations of γ may bear little information on the magnitude of OPL, because several factors contribute that are not taken into account in the calculations. Examples of these factors are the lifetime of excited singlet and triplet states in conjunction with laser pulse duration and quality, and concentration/medium effects,[48] which may involve intermolecular interactions between chromophores.

Other common aryl groups instead of thiophene also were considered in the design of OPL systems, with 1,9-substituted anthracene being one such example. Although 1,9-di(phenylethynyl)anthracene has a calculated γ value of 6.0×10^5 a.u., which is slightly greater than that of **5′**, this compound has considerable optical absorption in the region of 400–500 nm,[49] which made it less interesting for our OPL study.

AM1 semi-empirical calculations of a series of push–pull diaryl acetylenes have shown that twisting from the favored planar geometry to the conformation with orthogonal rings requires an energy of only 0.3 kcal mol^{-1}.[50] It was found also from MNDO-based calculations of the molecular first hyperpolarizability that the donor–acceptor interaction is still a dominant contribution even when the two phenyl rings are set orthogonally to each other.[50] We performed similar calculations of non-resonant γ using the TDHF/AM1 method to estimate the effect of inter-ring torsion in compound **5**. The geometry optimization of the conformation with the thiophene ring constrained orthogonal to both phenylene rings shows that this conformer has only 0.5 kcal mol^{-1} higher energy (ΔH_f) than that of the lowest energy, in which all three rings are coplanar. The former conformation has a value of γ that is 47% of the maximum. A third conformation of compound **5**, having one phenylene ring orthogonal to the two other rings, has ΔH_f and γ values intermediate to the other values. Furthermore, compound **7′** with the middle phenylene ring constrained in the calculations to be perpendicular to the adjacent rings, in both of the thiophene alkynyl substituents, has a γ value of 20.3×10^5 a.u., which is 58% of the value for the conformer having all rings coplanar. Although calculations at this level of theory are unreliable with respect to both energy and hyperpolarizability, it seems likely that compounds **5**–**7** will have a fairly wide distribution of conformations around the energy minimum at normal temperature, with different inter-ring torsion angles, but that γ will not be reduced severely because of that.

In recent work, we applied a chemometrics (partial least squares, PLS) approach for investigating relationships between non-linear absorption at 532 nm and readily accessible molecular ground-state parameters from DFT calculations.[51] For a set of 23 organic compounds and 41 initial variables, a model was found where six molecular properties were important for describing the optical limiting ability of the compounds. The parameters found to be relevant were: the number of electrons; the number of occupied molecular orbitals above -10 eV; the mean polarizability; the mean quadrupole moment; the total energy of the five highest occupied molecular orbitals; and the difference in energy between the five lowest unoccupied and five highest occupied molecular orbitals. The values of these parameters for compounds **5**–**7′** are, respectively: 148, 252, 356; 15, 25, 35; 321, 709, 1122; 111, 186, 259; 32.7, 31.1, 29.5 eV; and 30.0, 26.0, 22.4 eV, respectively. When going from **5′** → **6′** → **7′**, all six parameters change in the order predicted by the model to give better OPL.

Non-linear absorption measurements

The non-linear absorption of compounds **5**–**7** was recorded using 5 ns laser pulses at 532 nm (see Experimental). Values of the transmitted energy (I_{out}) as a function of the input energy (I_{in}) from the laser for THF solutions of compounds **5**–**7** are given in Table 2. A typical OPL curve of compound **5** is shown in Fig. 2. Generally, the OPL curves display a leveling of I_{out} at

Table 2. Experimental linear (T) and non-linear transmission data of 2,5-dialkynyl-substituted thiophenes **5**–**7** at 532 nm in THF solution

Compound	Conc. (M)	T (%)	I_{out} (μJ) at $I_{in} = 150$ μJ
5	1.2	76	4.2
	0.50	94	7
	0.10	98	12
	0.050	99	15
	0.010	>99	23
6	0.061	92	11.5
	0.010	99	16
7	0.018	97	13
	0.010	99	14

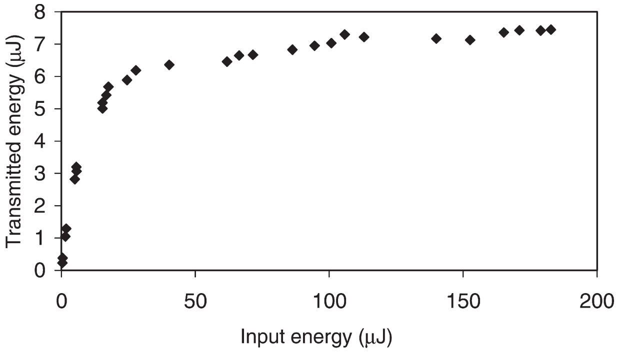


Figure 2. Optical limiting at 532 nm of 0.5 M thiophene **5** in THF

values of I_{in} in the range 100–150 μJ, but this leveling is not always complete to give a true clamping level. At even higher values of I_{in}, damage of the cuvet or the solute molecules occurs. For simplicity, the values of I_{out} are reported at $I_{in} = 150$ μJ in Table 2. The best OPL is found for the highest concentration (1.2 M) of compound **5**. Although a clamping level of ≤ 1 μJ for the transmitted light is preferred for good laser protection of eyes, the value of ~4 μJ is interesting in view of the simplicity of structure **5**. Compounds **6** and **7** could not be measured at such high concentration because of their limited solubility in THF. The maximum concentration of those two compounds was ~0.06 and ~0.02 M, respectively. However, a comparative study of 0.010 M solutions of compounds **5**–**7** showed increased optical limiting in the expected order $\mathbf{5} < \mathbf{6} < \mathbf{7}$ (Table 2).

Values of the linear transmission at 532 nm are also given in Table 2, showing good transparency of normal light at that wavelength even for the most concentrated sample of compound **5**. A transmission spectrum of compound **5** is shown in Fig. 3.

Additional work aimed at a better understanding of the mechanisms for OPL in this series of compounds is in progress.

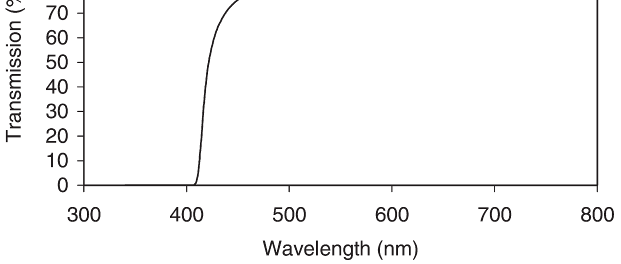


Figure 3. Linear transmission spectrum of 0.94 M thiophene **5** in THF

SUMMARY

The non-linear absorption at 532 nm of 0.01 M solutions of the arylalkynyl-substituted thiophenes increases from compound **5** to **6** and **7**, which shows that the extent of π-conjugation is important for the magnitude of the response, as expected. This is also indicated by γ values and other electronic parameters obtained from quantum chemistry calculations, but the magnitude of the OPL enhancement from compound **6** to **7** appears to be less than suggested by the calculations. The values of γ from AM1 TDHF calculations are somewhat greater for compounds **5**–**7** having alkyl groups than for the model compounds **5′**–**7′** that do not have alkyl groups. The γ values for **5′**–**7′** suggest that a larger increase of NLO effects is to be expected when going from **5′** to **6′** rather than from **6′** to **7′**. The same trend is noticed for compounds **5**–**7**, but the trend is less pronounced. Although the conformational space of the molecules was not fully explored, calculations on compounds **5** and **7′** reveal that twisting of one or two aryl rings relative to the other rings will not drastically decrease the γ values.

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REFERENCES

1. Kuzyk MG, Garvey DW, Vigil SR, Welker DJ. *Chem. Phys.* 1999; **245**: 533.
2. Frazier DO, Penn BG, Smith DD, Witherow WK, Paley MS, Abdeldayem HA. *Plast. Eng. (NY)* 1998; **49**: 693.
3. Stegeman GI. In *Nonlinear Optical Organic Molecular and Polymer*, Nalwa HS, Miyata S (eds). CRC Press: Boca Raton, FL, 1997; 799–812.
4. Zyss J. *Molecular Nonlinear Optics: Materials, Physics, and Devices*. Academic Press: Boston, 1994.
5. Shi S. *Contemp. Phys.* 1994; **35**: 21.
6. Kershaw S. *Opt. Eng. (NY)* 1998; **60**: 515.
7. Luther-Davies B, Samoc M. *Curr. Opin. Solid State Mater. Sci.* 1997; **2**: 213.
8. Köhler RH, Cao J, Zipfel WR, Webb WW, Hanson MR. *Science* 1997; **276**: 2039.
9. Birch DJS. *Spectrochim. Acta, Part A* 2001; **57**: 2313.
10. Cumpston BH, Ananthavel SP, Barlow S, Dyer DL, Ehrlich JE, Erskine LL, Heikal AA, Kuebler SM, Lee IYS, McCord-Maughon D, Qin JQ, Rockel H, Rumi M, Wu XL, Marder SR, Perry JW. *Nature* 1999; **398**: 51.
11. Van Stryland EW, Hagan DJ, Xia T, Said AA. In *Nonlinear Optical Organic Molecular and Polymer*, Nalwa HS, Miyata S (eds). CRC Press: Boca Raton, FL, 1997; 841–860.
12. Tutt LW, Boggess TF. *Prog. Quant. Electron.* 1993; **17**: 299.
13. Sun YP, Riggs JE. *Int. Rev. Phys. Chem.* 1999; **18**: 43.
14. Dini D, Barthel M, Hanack M. *Eur. J. Org. Chem.* 2001; **20**: 3759.
15. Reinhardt BA, Brott LL, Clarson SJ, Dillard AG, Bhatt JC, Kannan R, Yuan LX, He GS, Prasad PN. *Chem. Mater.* 1998; **10**: 1863.

16. Kannan R, He GS, Yuan LX, Xu FM, Prasad PN, Dombroskie AG, Reinhardt BA, Baur JW, Vaia RA, Tan LS. *Chem. Mater.* 2001; **13**: 1896.
17. Baur JW, Alexander MD Jr., Banach M, Denny LR, Reinhardt BA, Vaia RA, Fleitz PA, Kirkpatrick SM. *Chem. Mater.* 1999; **11**: 2899.
18. Perry JW. In *Nonlinear Optical Organic Molecular and Polymer*, Nalwa HS, Miyata S (eds). CRC Press: Boca Raton, FL, 1997; 813–840.
19. Paa W, Yang JP, Rentsch S. *Synth. Met.* 2001; **119**: 525.
20. Zhao M, Samoc M, Prasad PN, Reinhardt BA, Unroe MR, Prazak M, Evers RC, Kane JJ, Jariwala C, Sinsky M. *Chem. Mater.* 1990; **2**: 670.
21. Nalwa HS. In *Nonlinear Optical Organic Molecular and Polymer*, Nalwa HS, Miyata S (eds). CRC Press: Boca Raton, FL, 1997; 611–797.
22. Kamada K, Ueda M, Sakaguchi T, Ohta K, Fukumi T. *Chem. Phys. Lett.* 1996; **263**: 215.
23. Kamada K. *J. Phys. Chem. A* 2000; **104**: 4723.
24. Millefiori S, Alparone A. *Chem. Phys. Lett.* 2000; **332**: 175.
25. He GS, Xu GC, Prasad PN, Reinhardt BA, Bhatt JC, Dillard AG. *Opt. Lett.* 1995; **20**: 435.
26. Das GP, Dudis DS. *Chem. Phys. Lett.* 1999; **312**: 57.
27. Sahraoui B, Phu XN, Baldeck P, Nunzi J-M, Frere P, Roncali J. *Synth. Met.* 2000; **109**: 315.
28. Zhan X, Liu Y, Zhu D, Liu X, Xu G, Ye P. *Chem. Phys. Lett.* 2001; **343**: 493.
29. Yang JP, Paa W, Rentsch S. *Synth. Met.* 1999; **101**: 624.
30. Evans CH, Scaiano JC. *J. Am. Chem. Soc.* 1990; **112**: 2694.
31. Roussis SG, Proulx R. *Anal. Chem.* 2002; **74**: 1408.
32. Vincent D. *Nonlin. Opt.* 1999; **21**: 413.
33. Vincent D, Cruickshank J. *Appl. Opt.* 1997; **36**: 7794.
34. Dewar MJS, Zoebisch EG, Healy EF, Stewart JJP. *J. Am. Chem. Soc.* 1985; **107**: 3902.
35. *MOPAC-2000, Chem3D Pro 7.0*. Cambridge Soft Corp., Cambridge, MA.
36. Karna S, Dupuis M. *J. Comp. Chem.* 1991; **12**: 487.
37. Ridley JE, Zerner MC. *Theo. Chim. Acta* 1976; **42**: 223.
38. Zerner MC. In *Reviews in Computational Chemistry*, vol. 2, Boyd DB(ed). VCH: New York, 1991; 313–365.
39. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA, *Gaussian 98, Revision A. 4*. Gaussian: Pittsburgh, PA, 1998.
40. Becke AD. *J. Chem. Phys.* 1993; **98**: 5648.
41. Hehre WJ, Ditchfield R, Pople JA. *J. Chem. Phys.* 1972; **56**: 2257.
42. Hänninen E, Takalo H, Kankare J. *Acta Chem. Scand., Ser. B* 1988; **B42**: 614.
43. Mongin O, Gossauer A. *Tetrahedron* 1997; **53**: 6835.
44. Takahashi S, Kuroyama Y, Sonogashira K, Hagihara N. *Synthesis* 1980; **8**: 627.
45. Albota M, Beljonne D, Bredas JL, Ehrlich JE, Fu JY, Heikal AA, Hess SE, Kogej T, Levin MD, Marder SR, McCord-Maughon D, Perry JW, Rockel H, Rumi M, Subramaniam C, Webb WW, Wu XL, Xu C. *Science* 1998; **281**: 1653.
46. Cheng L-T, Wilson T, Marder SR, Stiegman AE, Rikken G, Spangler CW. *J. Phys. Chem.* 1991; **95**: 10643.
47. Wautelet P, Moroni M, Oswald L, Le Moigne J, Pham A, Bigot JY, Luzzati S. *Macromolecules* 1996; **29**: 446.
48. Riggs JE, Martin RB, Walker DB, Guo Z, Sun Y-P. *Phys. Chem. Chem. Phys.* 2004; **6**: 703.
49. Maulding DR, Roberts BG. *J. Org. Chem.* 1969; **34**: 1734.
50. Barzoukas M, Fort A, Klein G, Boeglin A, Serbutoviez C, Oswald L, Nicoud JF. *Chem. Phys.* 1991; **153**: 457.
51. Lind P, Lopes C, Öberg K, Eliasson B. *Chem. Phys. Lett.* 2004; **387**: 238.