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Novel functionalized oligo-vinylthiophene molecules with modulated second-order nonlinear optical response

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Abstract

We present a joint theoretical and experimental investigation of the second-order nonlinear optical properties of a new kind of active molecule with a triblock structure. The molecular architecture is such that two highly polarizable conjugated segments are separated from each other by a spacer; one of the conjugated segments is end-capped with an electron-donor group, the other one by an acceptor. E-vinylthiophenes are used as the conjugated segments; *N*,*N*-dimethylaniline and nitrophenyl are selected as the donor-acceptor pairs, while the spacer consists of a nonconjugated moiety. Several spacers are considered and discussed with respect to their ability to modulate the charge transfer between the donor and acceptor ends.

Keywords: Functionalized oligo-vinylthiophenes; Spacer-incorporated push-pull molecules; Second-order polarizability; Hyper-Rayleigh scattering; Quantum-chemical calculations

1. Introduction

Much effort is currently devoted to the search of π-conjugated chromophores with high and modulable nonlinear optical (NLO) responses. The NLO properties are based on the molecular second- and third-order polarizabilities and can lead to a wide range of optoelectronic or photonic applications such as high performance electrooptic modulators and all-optical switches [1–4]. Molecules with large NLO activities usually consist of an electron donor and an electron acceptor connected by a π-conjugated segment. Recently, a number of studies have suggested the possibility of promoting high polarizability by incorporating a spacer group within the conjugated pathway of push–pull compounds [5–9]:

At first sight, the interruption of conjugation induced by the spacer is expected to be detrimental for the obtention of significant polarizabilities, which usually requires efficient π-delocalization along the system. However, it is useful to recall the basis of the unified picture proposed for linear and nonlinear polarization in donor–acceptor conjugated molecules [10]. In such compounds, it has been established that the molecular polarizability of order n can be expressed as the first derivative of the polarizability of order $n — 1$ (or the molecular dipole moment if $n = 1$), with respect to a molecular structural parameter, such as bond-length alternation (BLA) or π-bond-order alternation (BOA), expressing the degree of ground-state polarization [10-13]. The incorporation of a spacer within the conjugated path can induce an abrupt modification of the molecular ground-state dipole moment as a function of varying the degree of ground-state polarization [7,8]; this leads to high values for the derivatives of the dipole moment and thus potentially to high polarizability [7,8].

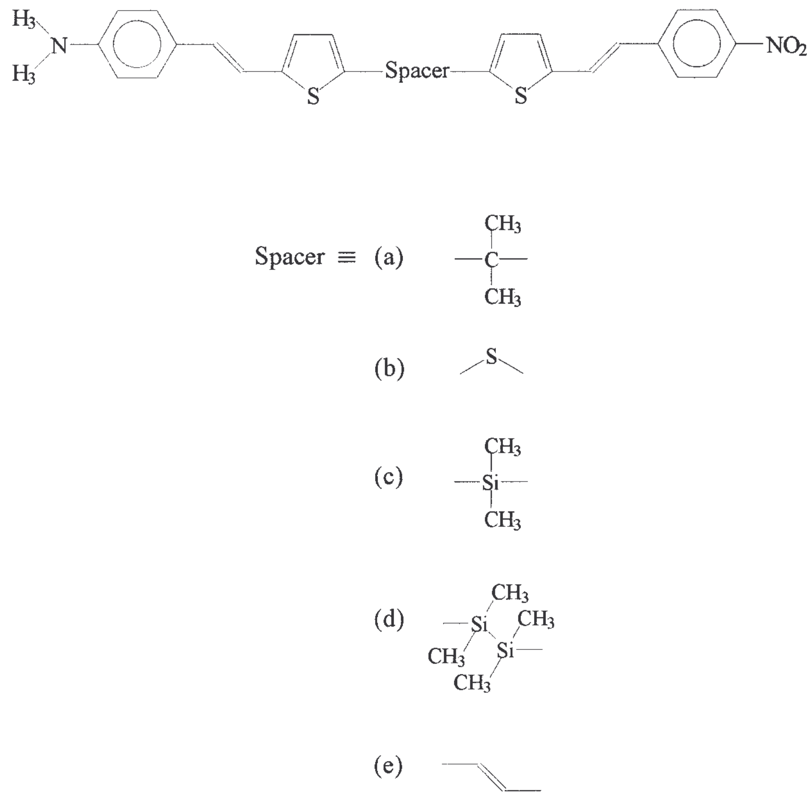


Fig. 1. Molecular structure of the compounds investigated in this work.

The model systems we have studied previously consist of a polyene-based molecular architecture, namely, a five double-bond polyene end-substituted by an amino donor group and an aldehyde acceptor group [7,8]; the thermal and photochemical stability of such molecules, however, hardly meet the criteria for practical applications. This contribution deals with the influence of spacers on the NLO properties of novel chromophores, whose synthesis has been recently reported [14], and with a theoretical and experimental investigation of the first hyperpolariz-ability β. These compounds consist of two E-vinylthiophene conjugated segments, one end-substituted by an electron-donor group (*N,N*-dimethylani-line) and the other by an acceptor group (nitrophenyl). These fully conjugated moieties are connected by a spacer; several spacers are considered, see Fig. 1: dimethylmethylene, sulfide, dimethylsilane, and tetra-methyldisilane; a completely conjugated system has also been analyzed for the sake of comparison (where the "spacer" is a vinylene group).

2. Methodology

2.1. Quantum-chemical calculations

The geometries of the molecules investigated in this work were optimized with the semiempirical AM1 Hartree–Fock method [15], which has also been used to estimate the second-order polarizabilities β via the finite-field approach [16]. The electronic structure (transition energies, atomic charges) was analyzed at the semiempirical INDO/SCI level (Intermediate Neglect of Differential Overlap Hamiltonian coupled with a Single Configuration Interaction) [17,18] on the basis of the AM1-optimized geometries (the electronic repulsion terms were expressed in terms of the Mataga–Nishimoto potential that best reproduces the transition energies within the INDO/ SCI formalism). The mono-excited configurations considered in the calculations have been generated by the promotion of an electron from one of the highest thirty occupied molecular orbitals to one of the lowest thirty unoccupied levels. We stress that previous studies have shown the suitability of semi-empirical CI techniques [19–30] and especially the INDO/SCI method [31–34] to evaluate the first- (α) and second-order (β) polarizabilities in organic molecules.

On the basis of the INDO/SCI description of the ground state and the excited states, we have calculated the static average linear polarizability (α) and the static and frequency-dependent β coefficients using the perturbative Sum-Over-States (SOS) approach [35]. Within SOS, the Cartesian components of the first- and second-order polarizabilities are given by:

$$\alpha_{ij} = 2\sum_{n\neq g}^{M}\sum_{i,j}\frac{\langle g|\mu_i|n\rangle\langle n|\mu_j|g\rangle}{E_{gn}} \qquad (1)$$

$$\beta_{ijk} = 6\sum_{m\neq g}^{M}\sum_{n\neq g}^{M}\sum_{i,j,k}\frac{\langle g|\mu_i|m\rangle\langle m|\bar{\mu}_j|n\rangle\langle n|\mu_k|g\rangle}{E_{gm}E_{gn}} \qquad (2)$$

where *i, j, k* denote Cartesian axes; $\langle g|\mu_i|n\rangle$is the electronic transition moment along the *i*-axis between the ground state$|g\rangle$ and the excited state $|n\rangle$; $\langle m|\bar{u}_i|n\rangle = \langle m|\mu|n\rangle - \langle g|\mu i|g\rangle)\delta_{mn}$ denotes the dipole moment difference between $|m\rangle$ and $|g\rangle$ in the case where $m = n$; E_{gm} is the energy difference between states $|m\rangle$ and . The summations over *M* are performed over the (900) excited states generated with the INDO/SCI method; this procedure provided converged values for α and *β*. The average value of the first polariz-ability ‹α› is defined as:

$$\langle\alpha\rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \qquad (3)$$

The dominators in the SOS formulae (Eqs. (1) and (2)) are modified when frequency-dependent polariz-abilities are evaluated; to obtain $\alpha_{ij}(-\omega, \omega)$, the denominator in Eq. (1) becomes:

$$E_{gn} - \hbar\omega - \mathrm{i}\Gamma_{gn} \qquad (4)$$

The second-harmonic generation terms ($\beta(-2\omega, \omega, \omega)$) are evaluated by changing the denominator in Eq. (2) to:

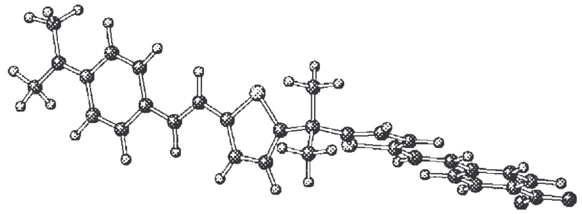
$$(E_{gn} - 2\hbar\omega - \mathrm{i}\Gamma_{gn})(E_{gm} - \hbar\omega - \mathrm{i}\Gamma_{gm}) \qquad (5)$$

In the above expressions, *β* is the frequency of the perturbating radiation field and T_{gn} is the damping factor associated with the transition to excited state *n›* (here taken to be 0.1 eV).

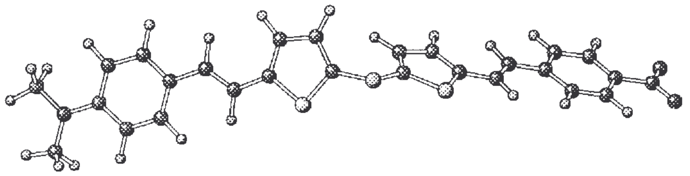
2.2. Experimental characterization

The optical first transition energies (λ_{max}) were determined by UV/Vis analysis of dilute solutions in chloroform with a Hitachi U-3300 spectrometer. The molecular second-order polarizabilities were measured with the Hyper-Rayleigh Scattering (HRS) technique [36,37], which provides information on the various components of the *β* tensor. In conjunction with the depolarization ratio in HRS, this information can be qualitatively compared to the calculated structure of the molecules, since their symmetry determines the number of nonzero as well as independent tensor components.

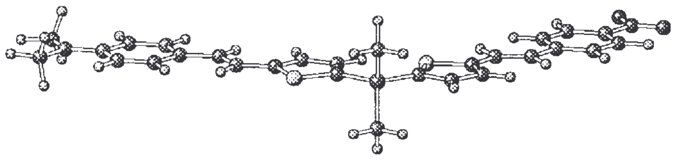
(a) θ = 75°



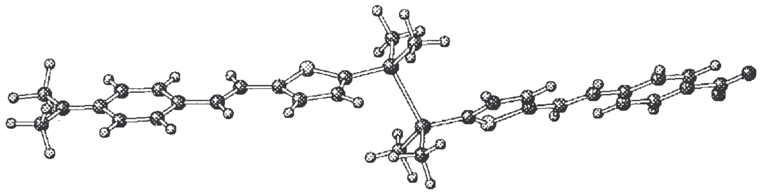
(b) θ = 59°



(c) θ — 0°



(d) θ = 2°



(e) θ = 0°

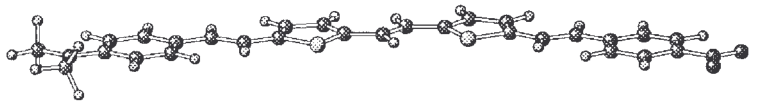
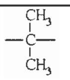
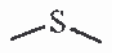
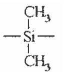
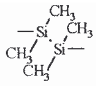


Fig. 2. Illustration of the AM1 most stable structure for the NLO-phores considered in this study: (a) spacer = $C(CH_3)_2$; (b) spacer = S; (c) spacer = $Si(CH_3)_2$; (d) spacer = $(–Si(CH_3)_2–)_2$; (e) "spacer" = vinylene moeity. The θ value represents the AM1-optimized dihedral angle between the average planes of the two thienylenevinylene conjugated segments.

Table 1
Static AM1-FF β tensor components and the β_{HRS} values (Eq. (6)) and measured HRS depolarization ratio factors. The β tensor components in italics are those that are at least 10% of the dominant tensor component β_{xxx}

Compound	Spacer	β_{xxx}	β_{yyy}	β_{zzz}	β_{xyy}	β_{xzz}	β_{zxx}	β_{zxx}	β_{zxx}	β_{zyy}	β_{xyz}	β HRS	Depolarization Ratio
1a		25.3	*14.9*	-0.9	*11.6*	0.2	0.3	-0.1	*2.7*	4.0	*2.6*	38.7	1.7
1b		88.9	—0.5	0.1	5.9	-1.7	-4.8	-0.6	2.2	0.4	1.7	88.2	3.6
1c		29.5	*7.9*	0.0	*11.8*	*27.7*	*8.2*	-0.5	0.0	0.0	0.0	40.2	2.2
1d		64.2	0.5	0.4	0.7	-0.5	0.2	0.0	-0.3	0.0	-0.9	59.8	2.5
1e		90.4	1.5	0.0	4.7	-0.1	12.1	0.1	0.0	0.0	0.0	87.4	3.5

A major advantage of the HRS technique is that it does not require the application of an electric field to orient the molecules, allowing the study of not only dipolar, but also octopolar molecules [38-40], as well as ionic species [41]; furthermore, no local field correction factor at dc frequency is necessary to estimate the β value. The HRS has also been used for the determination of second-order polarizabilities in mixed-valence metal complexes [42,43], proteins [44-46], and chiral compounds [47,48]. The pulsed laser source used in this study is an injection seeded Nd-YAG laser (@1064 nm).

The total scattering intensity expression for the HRS second-order polarizability β is:

$$\beta_{\mathrm{HRS}} = \sqrt{\frac{35}{6}\langle\beta_{\mathrm{HRS}}^2\rangle} \qquad (6)$$

where $\langle\beta_{\mathrm{HRS}}^2\rangle$ is defined as:

$$\langle\beta_{\mathrm{HRS}}^2\rangle = \frac{6}{35}\sum_i \beta_{iii}^2 + \frac{16}{105}\sum_{i\neq j}\beta_{iii}\beta_{ijj} + \frac{38}{105}\sum_{i\neq j}\beta_{ijj}^2 + \frac{16}{105}\sum_{ijk,\mathrm{cycl.}}\beta_{iij}\beta_{jkk} + \frac{20}{35}\beta_{ijk}^2$$

$$\text{with } i,j,k = x,y,z \qquad (7)$$

Both theoretical and experimental polarizabilities were calculated within a power series expansion of the dipole moment [49]. The depolarization ratio is given by:

$$\frac{I_v}{I_h} = \frac{\frac{5}{35}\beta_{xxx}^2 + \frac{18}{35}\beta_{xyy}\beta_{xxx} + \frac{27}{35}\beta_{xyy}^2}{\frac{1}{35}\beta_{xxx}^2 - \frac{2}{105}\beta_{xyy}\beta_{xxx} + \frac{11}{105}\beta_{xyy}^2} \qquad (8)$$

where the molecular axis parallel to the dipole moment is chosen as the x-axis, and the *y,* x-plane is the plane of the molecule.

3. Results and discussion

3.1. Geometrical structure

Fig. 2 is a sketch of the AM1-optimized structures of the various chromophores considered in this paper, along with the value obtained for the torsion angle between the two thienylenevinylene (coplanar) segments. Table 1 reports the calculated static /3 tensor components and β_{HRS} values (Eq. (6)) at the AM1-FF level, as well as the measured depolarization ratio factors. As mentioned above, this ratio can be used as a qualitative check of the optimized molecular structure: the higher the depolarization ratio, the more extended the molecule, and the more dominant the β_{xxx} component.

The completely conjugated NLO-phore 1e (see Fig. 2e) is characterized by a fully planar backbone and has a single major β_{xxx} tensor component due to its rod-like geometrical structure; this is consistent with the high depolarization ratio (3.5) measured in HRS.

Table 2 : Theoretical and experimental first optical transition energies, static first-order polarizabilities ($\alpha_{(o)}$), and static ($B_{HRS\ (0)}$) and frequency-dependent ($B_{HRS\ (1064\ nm)}$) second-order polarizabilities

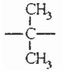
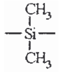
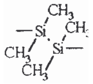
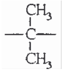
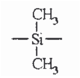
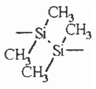
Compound	Spacer	THEORETICAL DATA				EXPERIMENTAL DATA		
		λ_{max} (nm)	$\langle\alpha_{(o)}\rangle$ (10^{-24}esu)	B_{HRS} (0) (10^{-30} esu)	$B_{HRS\ (1064\ nm)}$ (10^{-30} esu)	λ_{max} (nm)	$B_{HRS\ (0)}$ (10^{-30} esu)	$B_{HRS\ (1064\ nm)}$ (10^{-30} esu)
Ia		405	45.4	69.2	224.2	377	65	150
Ib		406	45.9	80.0	258.6	388	89	218
Ic		395	45.5	69.8	216.3	376	79	180
Id		407	48.8	86.4	296.0	380	124	290
Ie		500	65.7	174.4	2411.5	487	380	2980

Table 3 : Total Mulliken formal charges (expressed in |e|) calculated at INDO/SCI level for the three molecular segments (donor branch, spacer, acceptor branch) in the ground state (GS) and the first charge-transfer excited state (CT-ES) as well as the charge difference between the two states (A)

Compound	Spacer	GS			CT-ES			Δ		
		Donor branch	Spacer	Acceptor branch	Donor branch	Spacer	Acceptor branch	Donor branch	Spacer	Acceptor branch
Ia		–0.04	0.10	-0.06	-0.04	0.11	-0.07	0.00	0.01	-0.01
Ib		0.04	-0.05	0.01	0.05	-0.02	-0.03	0.01	0.03	-0.04
Ic		–0.10	0.23	-0.13	-0.09	0.24	-0.15	0.01	0.01	-0.02
Id		–0.09	0.22	-0.13	0.02	0.15	-0.17	0.11	-0.07	-0.04
Ie		0.02	0.02	-0.04	0.13	0.02	-0.15	0.11	0.00	-0.11

The spacers considered in this study have a distinct impact on the geometric (and electronic) molecular structures. For instance, the dimethyl methylene spacer (compound 1a) induces a very high torsion angle (75°) between the planes of the donor and acceptor segments, the angle between the long axes of the thienylenevinylene segments being at the tetra-hedral value of 109°. The overall low symmetry of the compound results in a large number of β tensor components contributing to the HRS signal, in agreement with the low depolarization factor value (1.7). On the other hand, the sulfide spacer, chromophore 1b, is characterized by a more extended geometrical structure, although the calculated dihedral angle between the two NLO moieties is not negligible (59°); the angle between the long axes of the two coplanar molecular segments actually approaches the value obtained for the completely conjugated reference NLO-phore 1e (135 vs. 145°, respectively). For this compound also, a single dominant (β_{xxx}) tensor component is observed, in agreement with the high depolarization ratio (3.6).

In the case of the dimethylsilane spacer 1c, the optimized geometry (Fig. 2c) is characterized by two coplanar thienylenevinylene segments that form an angle of 119° between their long axes. In the disi-lane chromophore 1d, the more stable structure displays two staggered parallel conjugated moieties oriented according to the direction of the molecular dipole moment (Fig. 2d). The structures of the 1c and 1d chromophores are thus consistent with the intermediate depolarization ratios of 2.2 and 2.5, measured by HRS.

3.2. Electronic structure and hyperpolarizability

In Table 2, we present the λ_{max} and /3 HRS experimental values (in chloroform) together with the corresponding theoretical INDO/SCI values. As expected, the structure of the spacer group strongly modulates the electronic absorption. There is a significant red shift for the fully conjugated system (Ie) with respect to the other molecules. The theoretical transition energies qualitatively reproduce the evolution of λ_{max} measured in chloroform; the absolute differences between the theoretical and experimental data are due, at least partly, to the fact that the calculations are performed on isolated molecules and do not incorporate solvent effects.

There is good qualitative agreement within the two theoretical approaches used to compute the β values; the AM1-FF values are found to be consistently 50— 60% of the SOS values, except in the case of the sulfide spacer system 1b, for which the AM1-FF β value is higher than the SOS one (this discrepancy is, in our experience, likely related to an overestimation of the polarization of sulfur-containing molecules in AM1 [50]). Hereafter, we therefore only discuss the SOS results in further detail. At the static limit, the SOS calculations reproduce the evolution of the HRS results for the triblock molecules well, with system 1e providing as expected the highest β value. The molecules 1a and 1c containing spacers of similar nature (dimethylmethylene and monosilane) are found to display similar β values, which are the lowest that have been obtained both theoretically and experimentally. The disilane spacer, and to a smaller extent the sulfide spacer, lead to higher β values; as discussed below, these spacers are the ones that allow for the transfer of some charge from the donor to the acceptor moiety. We emphasize that the HRS β obtained at 1064 nm for chromophore 1e is strongly enhanced by resonance, as a consequence of the long λ_{max} value (500 nm).

The role of the spacer in preventing charge transfer from the donor to the acceptor can be qualitatively assessed by considering the calculated charge population analysis. Table 3 shows the INDO/SCI total formal Mulliken charges calculated in each molecule for the three molecular segments that can be defined (the spacer moiety, the donor part, and the acceptor part); we give the charges in the ground state and in the lowest charge transfer excited state (CT-ES), as well as the charge difference between the two states. Charge transfer from the donor to the acceptor branch is limited in the ground state for all systems; actually, in the 1a, 1c and 1d molecules, charge is transferred from the spacer to both donor and acceptor moieties, whereas in the 1b molecule, the sulfide spacer receives a small amount of charge from both the donor and acceptor branches. The characteristics of the charge transfer in the CT-ES state are qualitatively the same as in the ground state for compounds 1a and 1c. For molecule 1b (sulfide spacer), a small charge transfer from the donor to the acceptor moiety is observed. In the disilane compound 1d, the acceptor branch receives a slightly higher amount of charge than in the ground state, transferred from both the spacer and the donor branch; the donor segment transfers 0.11 $|e|$ when going from the ground state to the CT-ES state, however, most of this charge goes to the spacer. In the fully conjugated system 1e, a charge of ca. 0.1 $|e|$ \flows from the donor to the acceptor segment. The charge difference between the GS and the CT-ES also confirms that charge delocalization along the whole molecule is limited for the systems containing a spacer in comparison with the fully conjugated molecule.

If we focus on the experimental B_{HRS} polarizabil-ities extrapolated at zero frequency, it is interesting to note that compounds 1a, 1b, and 1c display similar values, in the range of 65 - 90 × 10^{-30} esu. The disi-lane spacer, while preserving a low λ_{max}, around 380 nm, has a significantly higher β, 124 × 10^{-30} esu. A similar evolution in going from a mono-silane to a disilane spacer was also reported by Zyss and co-workers [5]. The disilane compound thus appears at first sight to have an attractive nonli-nearity-transparency trade-off [51]; a complete analysis of this trade-off would, however, require that the vibronic coupling be taken into account.

4. Synopsis

We have shown that the spacer incorporated into the triblock molecules effectively breaks the conjugation and lowers the wavelength of maximal absorption λ_{max} as well as the second-order polarizability with respect to the fully conjugated molecule. The structure of the bridge between the two conjugated segments, which we have characterized by the value of the dihedral angle between the two thienyleneviny-lene moieties, is found to depend on the nature of the spacer; the disilane spacer appears to be of special interest. The next step in this study would be to investigate the influence of solvent polarity on the NLO properties of these spacer-containing molecules; the goal there is to examine to what extent an abrupt change can occur in the dipole moment vs. medium polarity; such an abrupt change would indeed signal potentially large high-order polarizability values.

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