Second-order polarizability of donor–acceptor substituted oligothiophenes: substituent variation and conjugation length dependence

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Second-order polarizabilities and excited state dipole moments of a number of donor–acceptor substituted α-oligothiophenes have been investigated by use of electric field induced second harmonic generation (EFISH), solvatochromism and electrooptical absorption measurements (EOAM). The experimental results reveal that oligothiophenes are very effective conjugation units offering substantial enhancement of the second-order polarizability with increasing chain length.

1. Introduction

Conjugated organic molecules exhibit interesting physical and chemical properties, both from the fundamental point of view and for their application in data processing [1,2]. In recent years we have studied the photophysical properties of donor–acceptor substituted conjugated molecules [3]. As model systems we used polyenes as did others [4] because polyenes possess the greatest effective conjugation length. However, for the application the thermal and (photo)chemical stability of polyenes seem to be inadequate. More stable compounds which also exhibit extended conjugation are α-linked oligothiophenes [5,6]. For thiophene oligomers and polymers the application in electronic devices has already been demonstrated [7,8]. Indeed most work previously done has been focused on unsubstituted or alkyl substituted systems.

For an attractive application in nonlinear optics, however, such as for example frequency doubling or electrooptic modulation of light, donor–acceptor substituted conjugated molecules which exhibit charge dissymmetry, are required.

Systematic investigations of structure-property re-

lations of many donor–acceptor substituted organic π systems and their molecular second-order polarizabilities β have been carried out, e.g. benzenes, oligophenylenes, phenylpolyenes and diphenylpolyenes [4,9–15]. The largest values for second-order polarizabilities β have been obtained for long-chain polyenes containing amine donor and nitro or formyl acceptor groups [4,11–14]. For the oligophenylene series, in contrast, phenyl extension beyond the terphenyl is not worthwhile because of the rapid saturation of β [14,15].

Concerning thiophenes only few experimental data on second-order polarizabilities of some thiophene-phenylene systems exist [14,16]. So we synthesized a number of donor–acceptor substituted α-oligothiophenes DT_nA to investigate systematically the second-order polarizability of thiophene oligomers [17].
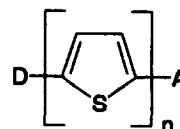
Scheme 1. Donor: D=MeO, MeS, Me$_2$N, PyN. Acceptor: A=NO$_2$, CHO. n=1–4.

Electron-donating substituents are methoxy, methylthio, dimethylamino and pyrrolidino (PyN) while the nitro and formyl groups are used as acceptor substituents. Second-order polarizabilities as well as ground and excited state dipole moments of these compounds were determined by means of electric-field induced second harmonic generation (EFISH) [18], solvatochromism [19,20] and electrooptical absorption measurements (EOAM) [21,22]. From the change of the dipole moment upon electronic excitation we estimate the charge transfer contribution of the lowest excited singlet state to the second-order polarizability using the two-state approximation [23].

2. Experimental section

All new compounds gave correct elemental analyses and spectral properties (^{1}H-NMR, ^{13}C-NMR, IR) in agreement with the assigned structures. 2-Methoxy-5-nitro-thiophene was prepared according to Sicé [24].

Absorption spectra were obtained in the range 200–800 nm using a Perkin-Elmer Lambda 7 spectrometer. The molar extinction coefficient κ was determined for n-hexane solutions applying the Lambert–Beer equation. For the solvatochromic determinations we used dried Merck Uvasol solvents.

The ground state dipole moments have been determined from dielectric measurements at 2 MHz using a WTM-DM 01 dipole meter and from refractive measurements for Na$_D$ light using a Milton Roy Abbe-3L refractometer. The dipole meter scale readings were calibrated and converted to dielectric constants by the use of n-pentane, n-hexane, cyclohexane, benzene and toluene as reference liquids. For each compound we measured 4–6 benzenic solutions at 20°C over the concentration range of the solute from 2×10^{-4} to 2×10^{-2} mol/ℓ.

All nitro substituted compounds exhibiting sufficient solubility in apolar solvents and showing no or negligible absorption at 532 nm were investigated by means of the EFISH technique [18]. Details of the device used in this work will be published elsewhere [25]. The EFISH results are relative to quartz ($d_{11} = 0.5$ pm/V [26]). The calibration was made under the same focal conditions as the solution mea-

surements, the quartz reference crystal being placed in the liquid cell volume and immersed in an index matching liquid. The mass fraction of the solution measurements was typically in the range 0–10^{-3}.

The electrooptical absorption apparatus has been described in ref. [27]. The solvents used in EFISH, dielectric and EOA measurements, cyclohexane, methylcyclohexane, tetrachloromethane, benzene and toluene were carefully dried and purified by rectification.

3. Theory

In many organic molecules of donor–acceptor type virtual transitions to the lowest excited singlet state ("charge transfer state") give the main contribution to the second-order polarizability β [23,28]. The charge transfer contribution can be written in the form

$$\beta_{CT}(\tilde{\nu}) = \beta_0 \frac{\tilde{\nu}_{ag}^4}{(\tilde{\nu}_{ag}^2 - \tilde{\nu}^2)(\tilde{\nu}_{ag}^2 - 4\tilde{\nu}^2)}, \qquad (1)$$

$$\beta_0 = \frac{3}{2h^2c_0^2} \mu_{ag}^2 (\mu_a - \mu_g) \frac{1}{\tilde{\nu}_{ag}^2}, \qquad (2)$$

where β_0 is the static second-order polarizability, μ_g and μ_a are ground and excited state dipoles, μ_{ag} the transition dipole, $\tilde{\nu}_{ag}$ the transition wavenumber, h Planck's constant, c_0 the speed of light in vacuum, and $\tilde{\nu}$ the wavenumber of the optical field.

The ground state dipole μ_g can be determined from dielectric and refractive measurements for several concentrations according to the Guggenheim–Smith equation [29]

$$\mu_g^2 = \frac{27kT\epsilon_0 M_2}{N_A} \frac{\alpha_\epsilon - \alpha_n}{\rho_1(\epsilon_1 + 2)^2}, \qquad (3)$$

with $\alpha_\epsilon = d\epsilon/dw_2$ and $\alpha_n = dn^2/dw_2$, ϵ being the relative permittivity and n the refractive index of the solution, w_2 and M_2 the mass fraction and the molar mass of the solute, ρ_1 and ϵ_1 the density and the relative permittivity of the pure (apolar) solvent, k Boltzmann's constant, T the temperature, ϵ_0 the permittivity of free space, and N_A Avogadro's constant.

The transition dipole μ_{ag} can be determined by numerical integration of the absorption band [19,20]:

$$\mu_{ag}^2 = \frac{3hc_0\epsilon_0 \ln 10}{2\pi^2 N_A} \frac{9n}{(n^2+2)^2} \int \frac{\kappa(\tilde{\nu})}{\tilde{\nu}} d\tilde{\nu}, \qquad (4)$$

wherein a Lorentz local field correction is included; κ is the molar decadic extinction coefficient of the solute.

All methods of determination of excited state dipoles μ_a are based on spectral shifts of the absorption band caused by an electric field, either external (electrochromism) or internal (solvatochromism) [19–22]. Solvatochromism has been treated by many authors [19,20,30]. Most treatments are based on the Onsager model [31], according to which the molecule is considered as a point dipole in a spherical solvent cavity with radius a and the solvent as a continuous dielectric body.

The general theory of solvatochromism [20] leads to expressions containing parameters which cannot be determined experimentally. Neglecting effects of polarizabilities and dispersion interactions on the solvent shift and assuming parallel ground and excited state dipoles one obtains the following equation [20]:

$$
\begin{aligned}
\tilde{\nu}'_{abs} &= \tilde{\nu}_{abs} + \frac{(\mu_a - \mu_g)^2}{4\pi\epsilon_0 a^3 h c_0} \frac{n^2 - 1}{2n^2 + 1} \\
&= \tilde{\nu}_0 - 2 \frac{\mu_g(\mu_a - \mu_g)}{4\pi\epsilon_0 a^3 h c_0} \frac{\epsilon - 1}{2\epsilon + 1} ,
\end{aligned}
\tag{5}
$$

where $\tilde{\nu}_{abs}$ and $\tilde{\nu}_0$ are wavenumbers of the absorption maxima in solution and gasphase, respectively, and $\tilde{\nu}'_{abs}$ is a short notation for the left-hand side (lhs) of the equation. With given values for the ground state dipole μ_g and the interaction radius a and a set of $\tilde{\nu}_{abs}$ data obtained for different solvents eq. (5) can be solved iteratively for $(\mu_a - \mu_g)$ by linear regression against the permittivity function $(\epsilon - 1)/(2\epsilon + 1)$. The poorly defined radius a is the main source for the uncertainty of solvatochromically determined excited state dipoles. In the present work we try to reduce this problem adjusting the interaction radius by comparison with excited state dipoles obtained from electrooptical absorption measurements (vide infra).

In EOA measurements one determines the effect of an external electric field on the absorption of linearly polarized light by a dilute solution of an organic dye [22]. The EOA spectrum is given by

$$
L\kappa/\tilde{\nu} = \frac{(\kappa^E/\tilde{\nu}) - (\kappa/\tilde{\nu})}{E_0^2} ,
\tag{6}
$$

where κ^E is the extinction coefficient of the solute in presence of the applied field. A regression analysis of the EOA spectrum yields information on ground and excited state dipoles and polarizabilities of the solute molecules as well as the direction $\boldsymbol{m}$ of the transition dipole in the molecule-fixed frame. For molecules with large ground state dipoles and large changes of the dipole upon electronic excitation explicit polarizability contributions and terms due to the field dependence of the transition dipole can be neglected. In this case the essential experimental information is contained in three regression coefficients, E, F and G, which we write for the purposes of this work in the form:

$$
E = (L_0^2/k^2 T^2)[3(\boldsymbol{m} \cdot \boldsymbol{\mu_g})^2 - \mu_g^2] ,
\tag{7}
$$

$$
F = (L_0^2/kT)\boldsymbol{\mu_g} \cdot (\boldsymbol{\mu_a} - \boldsymbol{\mu_g}) ,
\tag{8}
$$

$$
G = (L_0^2/kT)(\boldsymbol{m} \cdot \boldsymbol{\mu_g})[\boldsymbol{m} \cdot (\boldsymbol{\mu_a} - \boldsymbol{\mu_g})] ,
\tag{9}
$$

where $L_0 = (\epsilon_0 + 2)/3$ is the Lorentz local field factor for the static external field. In general Onsager local field factors are more appropriate [22]. Their application in the present work is not possible because of insufficient knowledge on the polarizability tensor of the investigated molecules.

With μ_{ga}^2 determined from the absorption spectrum using eq. (4) and $(\mu_a - \mu_g)$ obtained from either solvatochromism or electrochromism it is possible to estimate the CT contribution to the second-order polarizability according to eq. (1). In this approach one chooses the wavenumber of the band maximum for $\tilde{\nu}_{ag}$. However, electronic bands of organic molecules in liquid solution consist of several vibronic transitions and may be broad and strongly structured. In this case it is more satisfactory to combine eqs. (1), (2) and (4) into

$$
\beta_{CT}(\tilde{\nu}) = \frac{9\epsilon_0 \ln 10}{4\pi^2 h c_0 N_A} (\mu_a - \mu_g) \frac{9n}{(n^2 + 2)^2}
$$

$$
\times \int \frac{\kappa(\tilde{\nu}_{ag})}{\tilde{\nu}_{ag}} \frac{\tilde{\nu}_{ag}^2}{(\tilde{\nu}_{ag}^2 - \tilde{\nu}^2)(\tilde{\nu}_{ag}^2 - 4\tilde{\nu}^2)} d\tilde{\nu}_{ag} ,
\tag{10}
$$

where the integration is over the whole range of wavenumbers of the electronic band. It is assumed that the wavenumber $\tilde{\nu}$ lies in the preresonance regime where $\beta(\tilde{\nu})$ is a real quantity. With eq. (10) the dispersive enhancement of β is calculated with a correct spectral weighting since the experimentally de-

termined extinction coefficient κ ensures that the intensity profile (Franck–Condon progression) of the electronic band and the spectral broadening is properly taken into account.

In the EFISH experiment one utilizes a static external electric field E_0 to induce a second-order nonlinearity $d = \Gamma E_0$ in a liquid solution. The nonlinearity d is usually determined by non-phase-matched second harmonic generation applying the wedge technique [18]. For the molecules investigated in this work it is justified to assume Kleinman symmetry of the second-order polarizability tensor $\beta(-2\omega; \omega, \omega)$ and to neglect the dependence of β on the applied field $\gamma(-2\omega; \omega, \omega, 0)$. With these approximations one obtains the following equation for the experimental determination of the second-order polarizability:

$$L_{2\omega} L_\omega^2 L_0 \left(\frac{\mu_g \cdot \beta}{5kT} \right)$$

$$= \frac{\epsilon_0 M_2}{\rho_1 N_A} \left[\frac{\partial \Gamma}{\partial w_2} - \Gamma_1 \left(\frac{1}{3L_{2\omega}} \frac{\partial \epsilon_{2\omega}}{\partial w_2} \right. \right.$$

$$\left. \left. + \frac{2}{3L_\omega} \frac{\partial \epsilon_\omega}{\partial w_2} + \frac{1}{3L_0} \frac{\partial \epsilon_0}{\partial w_2} + \frac{1}{\rho_1} \frac{\partial \rho}{\partial w_2} - 1 \right) \right] \quad (11)$$

where $L_\Omega = (\epsilon_\Omega + 2)/3$, $\Omega = 0, \omega, 2\omega$, are Lorentz factors at the indicated field frequencies and $\beta_i = \sum_k \beta_{ikk}$ are components of the vector part β of the second-order polarizability. The terms in parenthesis correct for the dependence of the local field factors and of the density on the constitution of the phase; $\partial \rho / \partial w_2$ was neglected in the present work. A more general formulation of eq. (11) in terms of partial molar quantities will be given elsewhere [25].

4. Results and discussion

4.1. Evaluation

Fig. 1 shows the optical $(\kappa/\tilde{\nu})$ and electrooptical $(L\kappa/\tilde{\nu})$ spectrum of $Me_2NT_2NO_2$ in the region of the first allowed singlet excitation. The usual regression analysis [22] yields the EOA coefficients $E = (15030 \pm 270) \times 10^{-20}$ m^2 V^{-2}, $F = (5285 \pm 140) \times 10^{-40}$ C V^{-1} m^2 and $G = (5250 \pm 140) \times 10^{-40}$ C V^{-1} m^2. With eqs. (7)–(9) it follows $\mu_g = (26.7 \pm 0.3) \times 10^{-30}$ C m and $\mu_a = (73 \pm 2) \times 10^{-30}$

C m. From the equality of F and G, eqs. (8) and (9), it can be concluded that the dipole moments of the contributing excited vibronic states remain constant over the whole absorption band [22]. Therefore the excellent agreement of the experimental and approximated EOA spectrum suggests that there is only one intense electronic transition contributing in this spectral region.

The solvatochromism of $Me_2NT_2NO_2$ is shown in fig. 2 where the lhs of eq. (5) is plotted versus the permittivity function. A linear regression was performed for the solvent shifts represented by full points in fig. 2. The corresponding solvents have little or no specific type of interaction with the solute different from electrostatic dipole–dipole forces. Eq. (5) yields an excited state dipole which is in agreement with the EOA value (vide supra) setting $a = 0.69L$ where L is the radius of the smallest sphere enclosing the molecule. This choice of the interaction radius and the same set of solvents was equally applied to all other oligothiophenes studied in this work.

As seen in table 3, the agreement between data from EFISH measurements and the solvatochromic method is excellent for all thiophene oligomers compared.

For $Me_2NT_2NO_2$ the dispersion enhancement in the EFISH experiment seems to be somewhat underestimated by the two-level model (eq. (1)). Much better agreement can be obtained using eq. (10), where the dispersive enhancement is treated more exactly through integration over the whole absorption band. From the excellent agreement of both methods it can be concluded that the main contribution of the second-order polarizability arises from the low-lying charge transfer transition as it was supposed by the two-level model.

4.2. Comparison of bithiophenes with biphenyls and stilbenes

From the results given in tables 1 and 3 it is possible to compare the second harmonic generation efficiency of donor and acceptor groups in the bithiophene system. The efficiency of the donors increases in the order H, MeO, MeS, Me_2N, PyN. Nitro was found to be a more efficient acceptor than formyl in good agreement with results given for other π systems. With regard to the general observable correla-
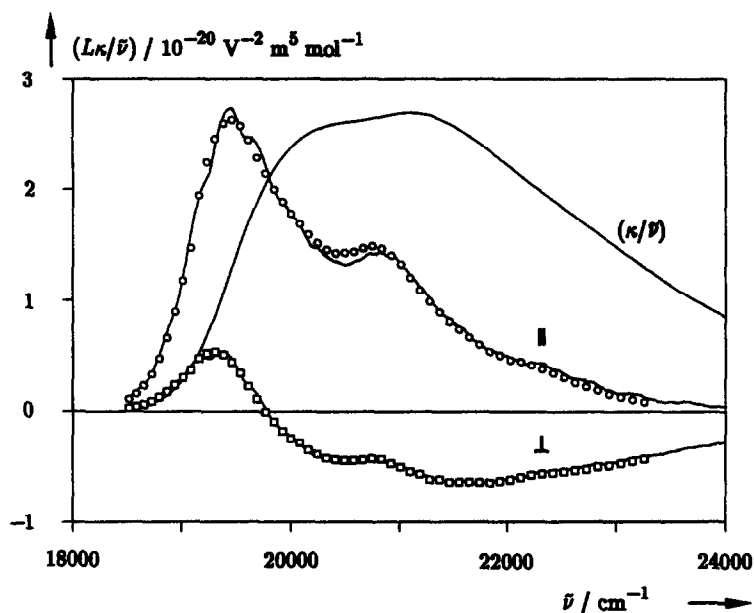
Fig. 1. Electrooptical absorption spectrum $(L\kappa/\tilde{\nu})$ of $Me_2NT_2NO_2$. The figure shows experimental data points for parallel ($\parallel$) and perpendicular ($\perp$) polarization of the incident light relative to the applied field and calculated curves obtained by a general linear least squares optimization. The definition of $(L\kappa/\tilde{\nu})$ is given in eq. (6). The absorption spectrum $(\kappa/\tilde{\nu})$ is displayed in arbitrary units. Solvent: cyclohexane, $T = 298$ K.

tion between β_0 and λ_{max} (see eq. (2)) it is interesting to note that $MeOT_2NO_2$ has a lower value for β_0 than $MeST_2NO_2$ despite of a longer wavelength absorbance. On the basis of the two-level model this can be explained from the much higher excited state dipole moment of $MeST_2NO_2$. Obviously for electron-rich heteroaromatics like thiophene the efficiency of rather weak donors like methoxy is diminished.

In table 4 static second-order polarizabilities of bithiophenes, biphenyls and stilbenes are summarized. For bithiophenes we have used our own EFISH data, for biphenyls and stilbenes we have used the EFISH data given by Cheng at 1910 nm [13,14]. The static coefficients are calculated by dividing the measured value by the relevant dispersion factor according to eq. (1). Because of the good agreement between our results for 4-dimethylamino-4'-nitrobiphenyl with the data given by Cheng, such a comparison seems reasonable. According to the two-level model solvents of greater polarity used by Cheng are expected to give somewhat higher values for β.

The results from table 4 suggest that bithiophenes exhibit much greater second-order polarizabilities

than biphenyls and nearly as great values as stilbenes, which are longer by one double bond. The high efficiency of bithiophenes for second harmonic generation is rationalized by the following reasons: (i) The reduction in CT transition energy according to the bathochromic effect of sulfur and to the partial elimination of the aromatic character in heteroaromatics. This reduced aromaticity favors quinonoid polyene-like structures and consequently better interaction of the end groups. (ii) The enhanced π overlap between thiophene units in comparison to phenylene units. In biphenyls the π overlap is reduced because of the steric interactions of the ortho-hydrogen atoms, whereas for α-bithiophenes hydrogens do not have any steric interaction in a coplanar trans-conformation (scheme 2).
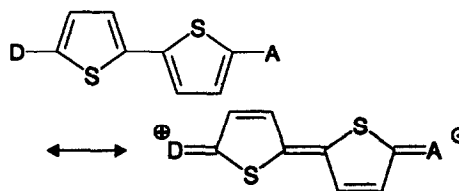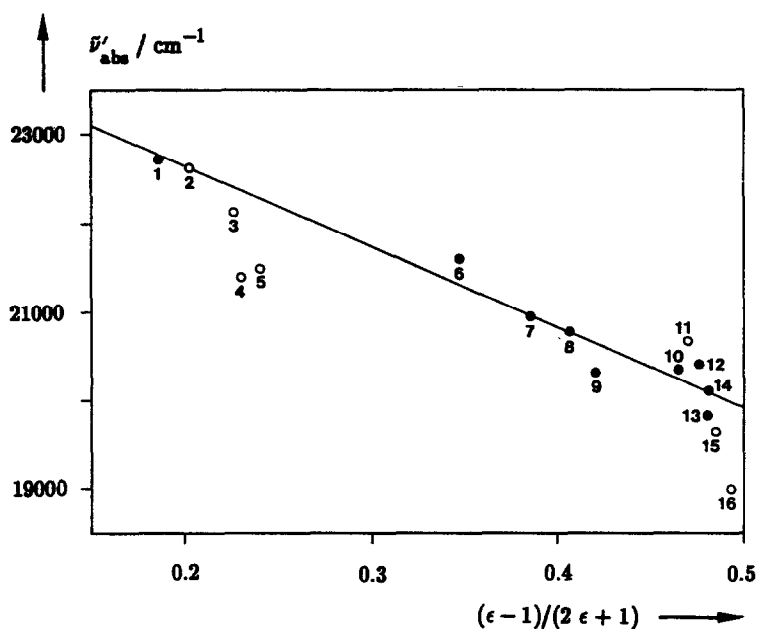

Scheme 2.

Fig. 2. Solvatochromism of $Me_2NT_2NO_2$. Solvents: (1) hexane, (2) cyclohexane, (3) tetrachloromethane, (4) benzene, (5) toluene, (6) diethyl ether, (7) ethyl acetate, (8) tetrahydrofurane, (9) dichloromethane, (10) acetone, (11) ethanol, (12) methanol, (13) dimethylformamide, (14) acetonitrile, (15) dimethylsulfoxide, (16) formamide. The linear regression was made for the solvents represented by full points. The definition of $\bar{\nu}'_{abs}$ is given in eq. (5).

Table 1
Dipole moments, absorption data and static second-order polarizabilities (β_{CT}) from solvatochromism of 2,2'-bithiophenes

D	A	μ_g [a]) (10^{-30} C m)	a (10^{-10} m)	μ_a (10^{-30} C m)	λ_{max} [b]) (10^{-9} m)	κ_{max} [b]) $(\text{m}^2 \text{ mol}^{-1})$	μ_{ag} [b]) (10^{-30} C m)	β_0 [c]) $(10^{-50} \text{ C m}^3 \text{ V}^{-2})$
H	NO_2	16.8	4.19	42	375	1750	16.2	3.5
MeO	NO_2	20.1	4.92	58	408	1930	17.0	7.0
MeS	NO_2	16.6	5.08	71	391	1830	17.8	10.0
Me_2N	NO_2	26.5	4.95	73 (73) [d])	466	2500	20.0	15.2
PyN	NO_2	28.1	5.48	83	499 (477) [e])	2700	19.9	20.8 (19.0) [e])
MeO	CHO	15.4	4.92	40	372	2270	17.6	4.0
Me_2N	CHO	19.7	4.95	57	421	2750	19.3	9.3
PyN	CHO	21.7	5.48	59	440	3310	20.5	11.4
$Me_2NB_2NO_2$ [f])		22.4	5.20	72 (80) [d),g])	375	2000	18.2	8.8

[a]) In benzene, experimental errors $\pm 0.2 \times 10^{-30}$ C m (10^{-30} C m = 0.2998 D).   [b]) In n-hexane.
[c]) According to eq. (2), in 10^{-50} C m³ V⁻² (= 2.6944×10^{-30} esu).   [d]) Electrooptical value.
[e]) Structure.   [f]) 4-Dimethylamino-4'-nitro-biphenyl.   [g]) Ref. [22].

An interesting aspect for applications arises from the large values of ground state dipole moments. For the case of electric-field poled polymers $\mu_g \cdot \beta$ has to be optimized instead of β [10]. This quantity seems to be even larger for bithiophenes than for stilbenes.

4.3. Effect of conjugation length

From the above reasons long-chain oligothiophenes are expected to have much greater second-order polarizabilities than bithiophenes. So we have

Table 2
Dipole moments, absorption data and static second-order polarizabilities (β_{CT}) from solvatochromism of oligothiophenes

DT$_n$A	μ_g [a] (10^{-30} C m)	a (10^{-10} m)	μ_a (10^{-30} C m)	λ_{max} [b] (10^{-9} m)	κ_{max} [b] (m^2 mol^{-1})	μ_{ag} [b] (10^{-30} C m)	β_0 [c] (10^{-50} C m^3 V^{-2})
MeOT$_1$NO$_2$	18.2	3.58	39	340	1180	12.4	1.4
MeOT$_2$NO$_2$	20.1	4.92	58	408	1930	17.0	7.0
MeOT$_3$NO$_2$	20.1	6.23	68	442	2500	20.5	15.0
MeOT$_4$NO$_2$	20	7.60	92	454	2950 [d]	24.2 [d]	33.0
PyNT$_2$NO$_2$	28.1	5.48	83	499 (477) [e]	2700	19.9	20.8 (19.0) [e]
PyNT$_3$NO$_2$	28	6.83	97	505	2360 [d]	23.1 [d]	35.2

[a] In benzene.   [b] In n-hexane.   [c] According to eq. (2).   [d] In dichloromethane.   [e] Structure.

Table 3
Second-order polarizabilities (β_z) of oligothiophenes and biphenyls measured by EFISH at 1064 nm

DT$_n$A	Solvent	λ_{max} (10^{-9} m)	$d\Gamma/dw_2$ (10^{-20} m^2 V^{-2})	$\beta_{1064\,nm}$ [c] (10^{-50} C m^3 V^{-2})	β_0 [d] (10^{-50} C m^3 V^{-2})	Solvatochromism (β_{CT})	
						$\beta_{1064\,nm}$ [e] (10^{-50} C m^3 V^{-2})	$\beta_{1064\,nm}$ [f] (10^{-50} C m^3 V^{-2})
HT$_2$NO$_2$	MCH [a]	378	4.8	6.9	3.0	8.2	8.1
MeOT$_2$NO$_2$	MCH	411	10.8	15	5.2	20	20
MeST$_2$NO$_2$	MCH	394	9.8	18	7.0	25	27
Me$_2$NT$_2$NO$_2$	MCH	472	103.0	118	20.1	91	112
MeOT$_1$NO$_2$	CCl$_4$	349	6.7	2.8	1.4	2.0	1.9
MeOT$_2$NO$_2$	CCl$_4$	418	29.1	17	5.6	22	21
MeOT$_3$NO$_2$	CCl$_4$	452	74.0	60	13.7	67	81
Hex$_2$NB$_2$NO$_2$ [b]	MCH	401	15.1	27	10.2	–	–
Me$_2$NB$_2$NO$_2$	toluene	400	35.6	33	12.2	–	–

[a] Methylcyclohexane.

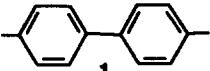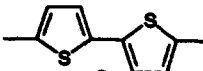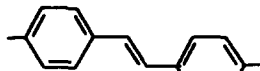[b] 4-Di-n-hexylamino-4'-nitro-biphenyl, $\mu_g = 24.9 \times 10^{-30}$ C m.

[c] Experimental value, errors 5–10%.

[d] Static second-order polarizability calculated from the experimental value using eq. (1).

[e] Two-state contribution to the second-order polarizability at 1064 nm estimated according to eqs. (1) and (2). μ_{ag} was determined from the absorption spectrum in the given solvent using eq. (4).

[f] Two-state contribution to the second-order polarizability at 1064 nm estimated according to eq. (10) from the absorption spectrum in the given solvent. μ_g and μ_a are listed in tables 1 and 2.

Table 4
Comparison of static second-order polarizability (β_0) of biphenyls (1), bithiophenes (2) and stilbenes (3) (EFISH data) [a]

D	A	1 in 1,4-dioxane [b]	2 in MCH [c]	3 in 1,4-dioxane [b]
H	NO$_2$	1.3	3.0	3.4
MeO	NO$_2$	2.9	5.2	8.6
MeS	NO$_2$	–	7.0	7.9
Me$_2$N	NO$_2$	14.8 [d]	20.1	20.6 [d]

[a] Calculated from the experimental value using eq. (1), in 10^{-50} C m^3 V^{-2} ($= 2.6944 \times 10^{-30}$ esu).

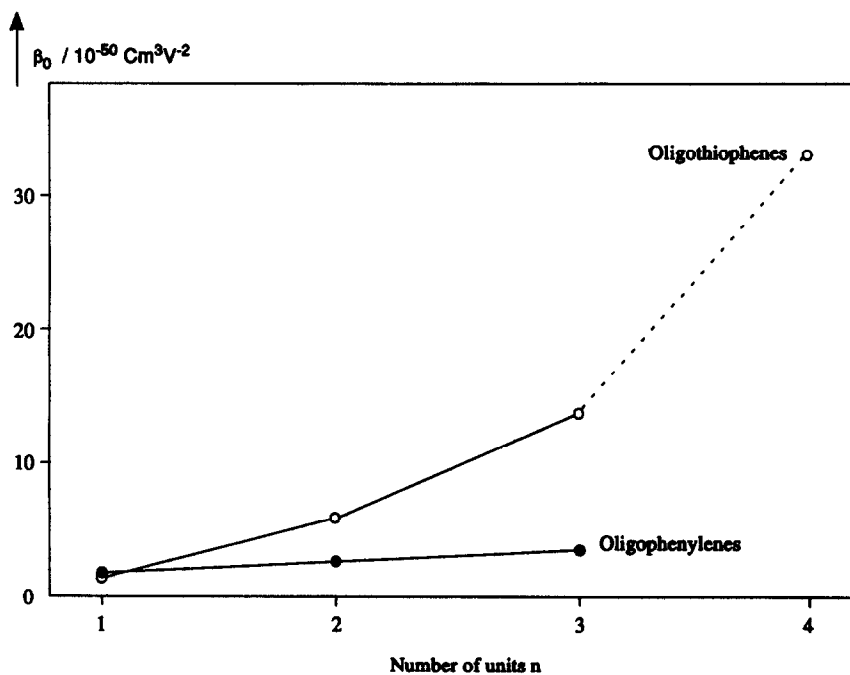[b] Refs. [13,14].   [c] MCH = methylcyclohexane.   [d] In chloroform.

Fig. 3. Effect of increasing chain length n on the static second-order polarizability β_0 of MeOT$_n$NO$_2$ in comparison to MeOB$_n$NO$_2$ [14]. The data point for oligothiophenes ($n=4$) was obtained from solvatochromism.
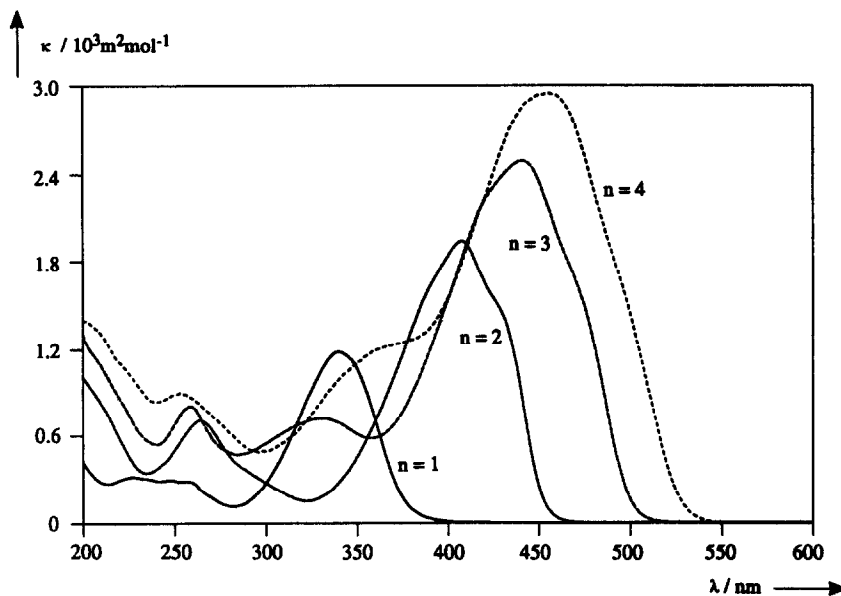

Fig. 4. UV/vis absorption spectra of MeOT$_n$NO$_2$ in n-hexane solution. κ is the molar decadic extinction coefficient.

studied the dependence of β_0 on the number of repeat units, n, for methoxy-nitro substituted thiophene oligomers with $n = 1$–4 (fig. 3). For the methoxy and nitro end groups experimental data on chain dependence are also available for diphenylpolyenes and oligophenylenes [12,14]. Whereas for diphenylpolyenes no saturation of β_0 is observed for up to 9 double bonds, in oligophenylenes β_0 maximizes between bi- and terphenyls, which was explained by constraints on π overlap and the high degree of aromatization of the phenyl unit [14]. In fig. 3 our results on chain dependence for oligothiophenes are compared to oligophenylenes.

For up to 8 double bonds no saturation of β_0 is observed for thiophene oligomers. Like polyenes oligothiophenes show a substantial increase of β_0 with the number of double bonds. From logarithmic plots of β_0 versus n we get for $MeOT_nNO_2$ $\beta_0 \sim n^{2.1}$ (EFISH, $n = 1$–3), $\beta_0 \sim n^{2.2}$ (solvatochromism, $n = 1$–4). For

Similar trends are also found for the maximum absorption wavelengths λ_{max} as as function of conjugation units n (fig. 4).

Whereas CT transitions of oligothiophenes like polyenes bathochromically shift with increasing chain length, in oligophenylenes absorption wavelength maximizes again for bi- or terphenyls [14,15,32]. In summary our results on chain dependence prove oligothiophenes to be excellent conjugation units allowing intense interactions of the end groups.

5. Conclusion

We have studied second-order polarizabilities of a new series of interesting nonlinear optical organic molecules applying the EFISH technique, solvatochromism and electrooptical absorption measurements.

The superiority of the thiophene unit over the phenyl unit was demonstrated, since thiophenes exhibit greater efficiencies per unit molecular volume than systems containing the phenyl unit.

The results on chain length dependence suggest that oligothiophenes are much more comparable to polyenes than to oligophenylenes with regard to their optical and nonlinear optical properties.

Because of the favorable interaction of large second-order polarizabilities and dipole moments do-

nor–acceptor substituted oligothiophenes are recommended as interesting candidates for applications in poled polymers.

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