Structure – Second-Order Polarizability Relationship in Chromophores Incorporating a Spacer: A Joint Experimental and Theoretical Study

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Abstract: A joint theoretical and experimental study is reported on the structure – polarizability relationship in a novel type of push – pull conjugated system which contains a spacer within the conjugated backbone. The chromophores are based on a dithienyl conjugation pathway, spaced by a keto group, and selectively end-capped by a donor and an acceptor. Four chromophores were synthesized, in which the strength of the acceptor group and the length of the conjugated path were varied. The electronic properties of two model compounds were studied theoretically by means of correlated quantum-chemical calculations. The degree of ground-state polarization was varied in the calculations by the application of an external electric field and varied experimentally by the modification of the dielectric constant of a binary mixture of solvents. The linear and nonlinear optical properties of the compounds (measured in solution by hyper-Rayleigh scattering) are discussed in detail.

Keywords: donor – acceptor systems · ketones · nonlinear optics · semiempirical calculations · solvent effects

Introduction

A key objective in the development of materials for electro-optical applications is to find highly active chromophores with large second-order polarizabilities β. The classical molecules that have large nonlinear optical (NLO) activities usually contain an electron donor and an electron acceptor connected by a π-conjugated segment.[1, 2] Although polyenes are the most effective π-conjugated systems, their thermal and photochemical stability is not high enough for practical applications; on the other hand, the large aromaticity of the benzene ring[2, 3] has a detrimental effect on β. Since the ground-state aromaticity of thiophene is lower than that of benzene and the solubility of thiophene derivatives is usually higher than that of the parent benzene compounds, much attention has recently been paid to chromophores that contain thiophene[4–6] (this has led to the appearance of the first commercial organic-based electro-optical device[7]).

For many applications, compounds are required that combine high nonlinear optical activities with a wide transparency window.[8] One route that has been followed in order to improve on the transparency – efficiency trade-off was the introduction of a silane or disilane group as a spacer in the center of the conjugated bridge;[9, 10] the role of this spacer is to modulate the conjugation between the donor and acceptor termini. Such compounds were found to be transparent above $\nu = 360$ nm; however, their second-order polarizabilities are rather low. Quantum-chemical calculations have indicated that push – pull polyenes containing a (di)methylene spacer group that interrupts the conjugation along the molecule could induce large hyperpolarizabilities;[11] these are, however, correlated to very low first optical transition energies. More recent calculations suggest that the use of a carbonyl (ketone) function as a spacer could produce a compromise: high polarizabilities without an overly large decrease in the bandgap energy.[12]

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Here, we report on a theoretical and experimental study of the effect of the solvating medium on the linear and nonlinear optical properties of push–pull systems in which the π-conjugated core (composed of two thiophene rings) is modulated by a carbonyl spacer (Figure 1). This choice of chemical structure potentially combines the advantages of: i) the incorporation of the promising carbonyl spacer; ii) the well-known properties of the thiophene ring in terms of thermal stability and decreased aromaticity, as discussed above, and iii) their suitability as guests in polymer host matrices for electro-optical applications. Note that the solvatochromic[13] and second-harmonic generation (SHG) properties of similar chromophores based on bis(benzylidene)cycloalkanones[14a, b] have already been described; however, since the latter compounds present a nearly centrosymmetrical structure, the SHG signal is weak. The nonlinear properties of some thienylchalcone molecules have also been investigated;[14c, d] for example, 1-(2-thienyl)-3-(4-methylphenyl)propene-1-one displays a SHG signal 15 times as large as that of urea.

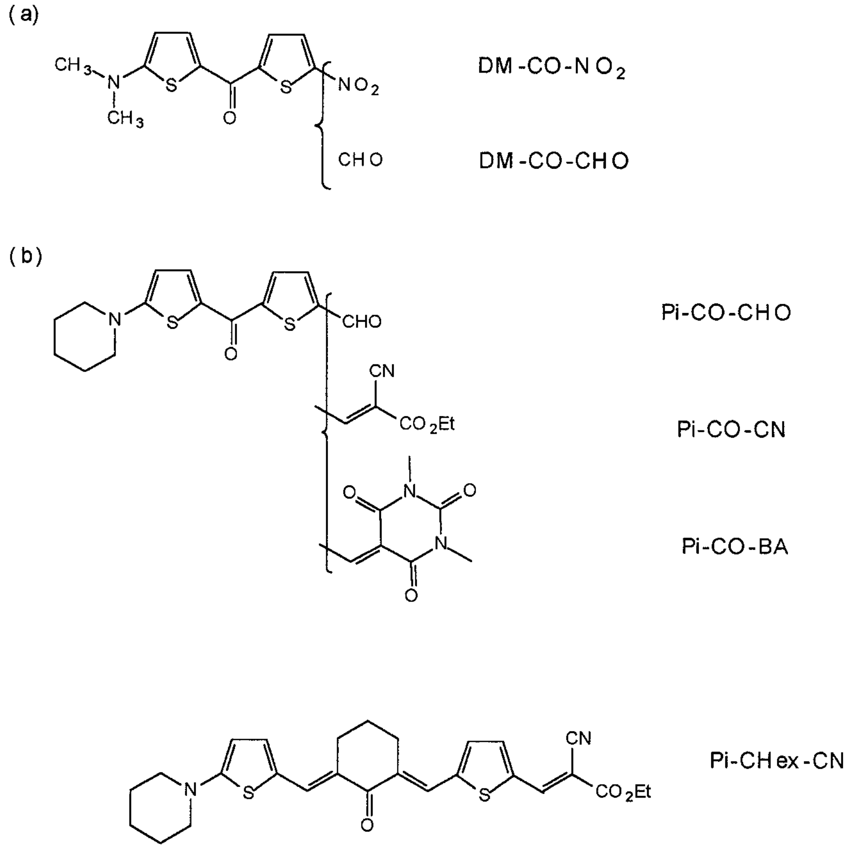


Figure 1. Molecular structures of the compounds studied theoretically.

This paper is organized as follows. Firstly, a theoretical evaluation is presented of the influence of a reaction field on the model chromophores 5-(5-*N*,*N*-dimethylamino-2-thienylcarbonyl)-2-nitrothiophene (DM-CO-NO$_2$) and 5-(5-*N*,*N*-dimethylamino-2-thienylcarbonyl)-2-thiophenecarbaldehyde (DM-CO-CHO) (Figure 1a). The second part focuses on the experimental study of the compounds shown in Figure 1b, that is, 5-(5-piperidino-2-thienylcarbonyl)-2-thiophenecarbaldehyde (Pi-CO-CHO), ethyl (*E*)-2-cyano-3-[5-(5-piperidino-2-thienylcarbonyl)-2-thienyl]-2-propenoate (Pi-CO-CN), 1,3-dimethyl-5-[5-(5-piperidino-2-thienylcarbonyl)-2-thienylmethylene]hexahydro-2,4,6-pyrimidinetrione (Pi-CO-Ba), ethyl (*E*)-2-cyanomethyl-3-{5-2-oxo-3-[(*E*)-1-(5-piperidino-2-thienylmethylidene)cyclohexylidenemethyl]-2-thienyl}-2-propenoate (Pi-CHex-CN); a detailed synthesis of these carbonyl-spaced chromophores is given. In the case of Pi-CO-CN, we describe the experimental development of the charge-transfer absorption band in solution (solvatochromism was determined with UV/Vis spectroscopy) and the molecular hyperpolarizability (determined with hyper-Rayleigh scattering) as a function of the polarity of the solvent; the polarity was controlled by mixing toluene and DMSO, two solvents with almost identical refraction indices but very different dielectric constants. We investigated the effect of the acceptor strength and π-conjugation pathlength on the molecular hyperpolarizability for the carbonyl-spaced chromophores in solution. Finally, a discussion of the theoretical results is presented in correlation with the experimental data.

Results and Discussion

Theoretical study:

Methodology: The compounds DM-CO-NO$_2$ and DM-CO-CHO (Figure 1a) provide adequate and simple models for Pi-CO-CN and Pi-CO-CHO, respectively (Figure 1b). The *N*,*N*-dimethylamino and piperidino groups have comparable electrodonating strengths, while the nitro and vinyl cyanoacetate groups can be considered as having comparable electroacceptor strengths.[2a]

The methodology used here is the same as that used in a number of previous reports;[15, 11, 12] it allows us to compare the results obtained here on compounds which contain a spacer with those obtained earlier on fully conjugated systems. The procedure consists of three steps:

1) Geometry optimizations are carried out with the help of the semiempirical Hartree–Fock INDO (intermediate

neglect of differential overlap) method.[16, 17] A homogeneous static electric field (***F***) in the range $10^7 - 10^8\,\mathrm{V\,cm^{-1}}$ is applied to tune the degree of ground-state polarization[18a] (we note that this range in ***F*** values is comparable to the reaction fields associated with common dipolar solvents; for example, the reaction field in chloroform is $0.9 \times 10^7\,\mathrm{V\,cm^{-1}}$ and that in nitrobenzene is $4.3 \times 10^7\,\mathrm{V\,cm^{-1}}$).[18b] Note that the results we present were obtained assuming a fully planar structure for all systems: since the optimal torsion occurring around the ketone bridge is calculated to be small (≈18°) and to be largely independent of the applied electric field, it is more convenient to use a planar conformation in order to provide electronic properties, such as π-bond orders, more easily.

2) The electronic structure (state dipole moments, transition energies, and transition dipole moments between states) is evaluated with the INDO method coupled to a configuration interaction scheme that takes account of single and double excitations[16] (single excitations between all π orbitals; double excitations between the five highest occupied π MO's and the five lowest unoccupied π* MO's).
3) On the basis of the state characteristics, the static and dynamic values of the first- and second-order polarizabilities, α and β, are calculated within the sum-over-states method (SOS) derived from the perturbation theory.[19] The summations are performed over 50 states, which provides convergent values for the molecular polarizabilities of the compounds investigated here. For the dynamic calculations, the damping factor associated with the excited states is set at 0.2 eV.

It should be borne in mind that the application of a homogenous external electric field (rather than the application of the self-consistent reaction field technique[20]) to the molecules allows us to modulate the evolution of the degree of ground-state polarization in the molecule from a neutral structure to a fully charge-separated zwitterionic structure. We stress that only a part of this evolution is expected to be observed experimentally, since the actual reaction fields in solution are smaller than the largest external fields we apply.[20, 21]

Both theoretical and experimental polarizabilities are calculated within a power series expansion of the dipole moment.[18c] We recall that the average value of the first-order polarizability α is defined as $\langle\alpha\rangle = \frac{1}{3}(\alpha_{\mathrm{xx}} + \alpha_{\mathrm{yy}} + \alpha_{\mathrm{zz}})$. In order to obtain a better comparison between the theoretical and experimental values of the hyper-Rayleigh scattering (HRS), we have calculated the second-order polarizability β with the HRS expression in Equation (1),[22] where $\langle\beta^2_{\mathrm{HRS}}\rangle$ is defined by Equation (2) with $i, j, k = x, y, z$.

$$\beta_{\mathrm{zzz}} = \sqrt{\frac{35}{6}\langle\beta^2_{\mathrm{HRS}}\rangle} \tag{1}$$

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

Results: Figure 2 illustrates the evolution of the formal total charge in the ground state as ***F*** increases for the individual molecular segments (donor, spacer, acceptor) within DM-CO-NO_2. The external electric field is oriented in such a way as to promote charge transfer from the donor segment to the acceptor segment. We observe that the charge flow increases continuously as a function of ***F*** along the whole molecule; the three segments of the molecule actively participate in the charge transfer for any value of the electric field. This confirms that the carbonyl spacer does not strongly interrupt the charge delocalization between the terminal donor and acceptor segments.[12] However, two regimes can be distinguished in the charge transfer evolution depicted in Figure 2. The first regime, from 0 to $\approx 6 \times 10^7\,\mathrm{V\,cm^{-1}}$, is mainly associated with a flow of charge from the donor segment to the carbonyl spacer group; the spacer is acting as the main acceptor group and only a small amount of charge is transferred through the spacer towards the NO_2 acceptor segment. In the second regime (beyond $6 \times 10^7\,\mathrm{V\,cm^{-1}}$) the acceptor role of the spacer saturates and a substantial charge transfer occurs through the spacer from the donor to the NO_2 acceptor segment.

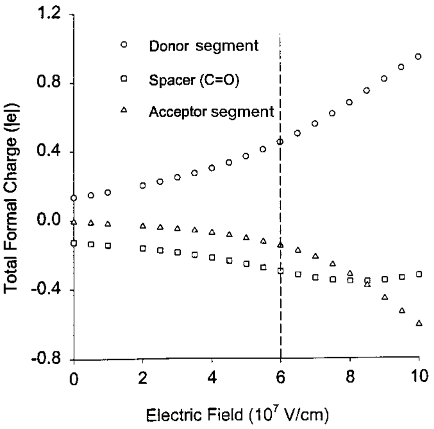
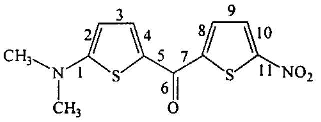


Figure 2. Evolution, as a function of the applied electric field, of the INDO-SDCI total formal charge in the ground state per moiety of the DM-CO-NO_2 compound (the donor/acceptor segments contain the adjacent thiophene ring).

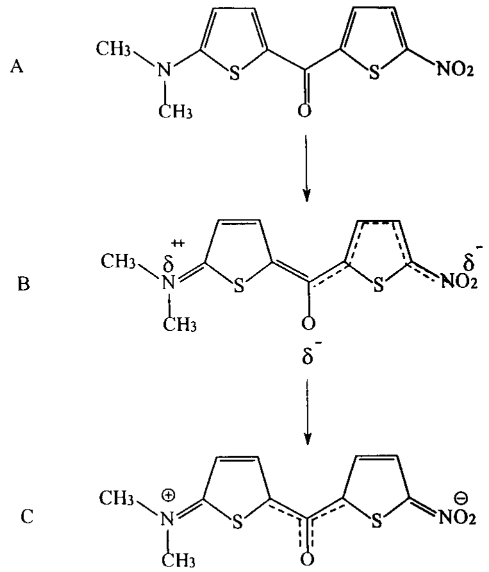
In this semiconjugated system (considered to be planar for all values of ***F***), it is convenient to depict the change in geometry induced by the charge redistribution by considering the evolution of the π-bond orders (π-BO) with respect to ***F*** (note that the value of π-BO = 0 corresponds to a purely σ-bond, while π-BO = 1 is related to a purely double π-bond). In Table 1, we present the π-BOs in the DM-CO-NO_2 molecule for values of ***F*** ranging from 0 to $10^8\,\mathrm{V\,cm^{-1}}$. Charge transfer leads to a reduction in the π-BOs for the initially double bonds and an increase for the single bonds. When comparing the π-BOs of the two bonds connecting the donor and acceptor groups to the conjugated pathway (bonds 1 and 11, respectively, see labeling in Table 1), bond 1 (donor segment) is affected twice as much as bond 11 (acceptor counterpart) when ***F*** increases from 0 to $6 \times 10^7\,\mathrm{V\,cm^{-1}}$; on the other hand, for ***F*** values beyond $6 \times 10^7\,\mathrm{V\,cm^{-1}}$, the two bonds present the same change in π-BO value (the same statement can be made for the other corresponding bonds of the molecule). This evolution of the π-BOs is thus fully consistent with the analysis of the charge redistribution in the ground state which

Table 1. π-Bond orders in the ground state of the DM-CO-NO_2 calculated with INDO-SDCI.



F	Donor segment					C=O	Acceptor segment				
[10^7 V cm^{-1}]	1	2	3	4	5	6	7	8	9	10	11
0	0.446	0.785	0.457	0.798	0.406	0.746	0.292	0.853	0.414	0.842	0.312
2	0.495	0.745	0.504	0.754	0.455	0.718	0.285	0.852	0.421	0.829	0.336
4	0.555	0.692	0.566	0.695	0.515	0.680	0.284	0.845	0.435	0.809	0.368
6	0.627	0.620	0.644	0.618	0.583	0.627	0.295	0.827	0.462	0.777	0.409
8	0.707	0.535	0.727	0.534	0.643	0.564	0.329	0.788	0.511	0.727	0.469
10	0.781	0.452	0.792	0.471	0.667	0.506	0.394	0.724	0.584	0.655	0.549

occur from the donor segment to the acceptor segment. A schematic representation of the evolution of the molecule upon application of the external electric field is presented in Scheme 1 and Figure 3.



Scheme 1. Evolution of the geometric structure as a function of ground-state polarization in keto-spaced chromophores: from the neutral form **A** to zwitterion-like forms **B** and **C**.

The charge transfer in the ground state can also be characterized by the evolution of the ground-state dipole moment (Figure 3). Beyond a field of 6×10^7 V cm^{-1}, a more abrupt increase in the dipole moment occurs, in agreement with a redistribution of the charge over the whole molecule from the donor end to the acceptor end. The evolutions of the first- and second-order polarizabilities with respect to ***F*** are also given in Figure 3. The derivative relationships among the polarizabilities are correctly reproduced by our calculations; for instance, it can be seen that the α curve peaks and the β_{HRS} curve vanishes in DM-CO-NO_2 at the same value of ***F*** ($\approx 8.5 \times 10^7$ V cm^{-1}). In agreement with the evolution behavior of the ground-state dipole moment discussed above, a smooth increase was found in the first-order polarizability for the weaker field values (ranging from 0 to $\approx 6 \times 10^7$ V cm^{-1});

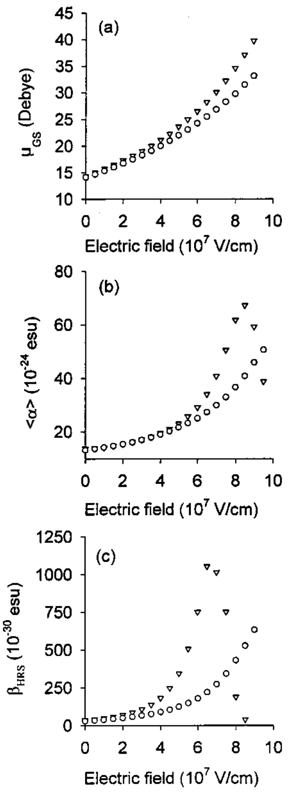
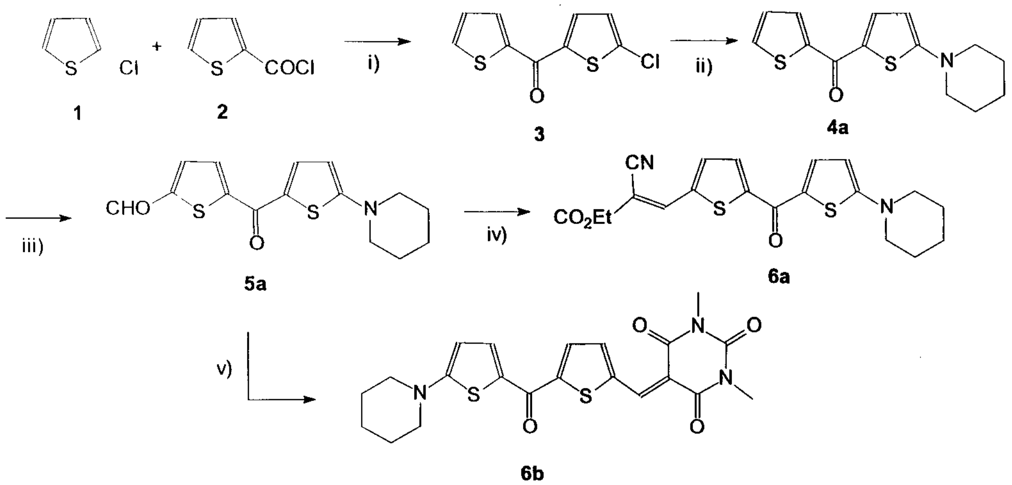


Figure 3. INDO-SDCI/SOS calculated evolution of: a) the ground-state dipole moment, b) the average first-order polarizability ($\langle\alpha\rangle$), and c) the second-order polarizability (β_{HRS}) as a function of the applied electric field in DM-CO-NO_2 (▽) and DM-CO-CHO (○).

beyond 6×10^7 V cm^{-1}, the evolution is more rapid since a substantial amount of charge is transmitted through the spacer. The peak value of β_{HRS}, obtained at $\approx 6.5 \times 10^7$ V cm^{-1}, is $\approx 1 \times 10^3 \times 10^{-30}$ esu; we note that this value is not as high as the those previously calculated for a push–pull polyene containing a methylene or dimethylene spacer[11, 12] ($\approx 10^5 \times 10^{-30}$ esu); however, in these compounds the first optical transition is of the order of a few tenths of an eV. In the case of DM-CO-NO_2, the peak value for β is related to a transition energy at ≈ 1.25 eV.

The DM-CO-CHO molecule displays a lower hyperpolarizability β compared to DM-CO-NO_2 (Figure 3). This illustrates the influence of the donor/acceptor strength on the



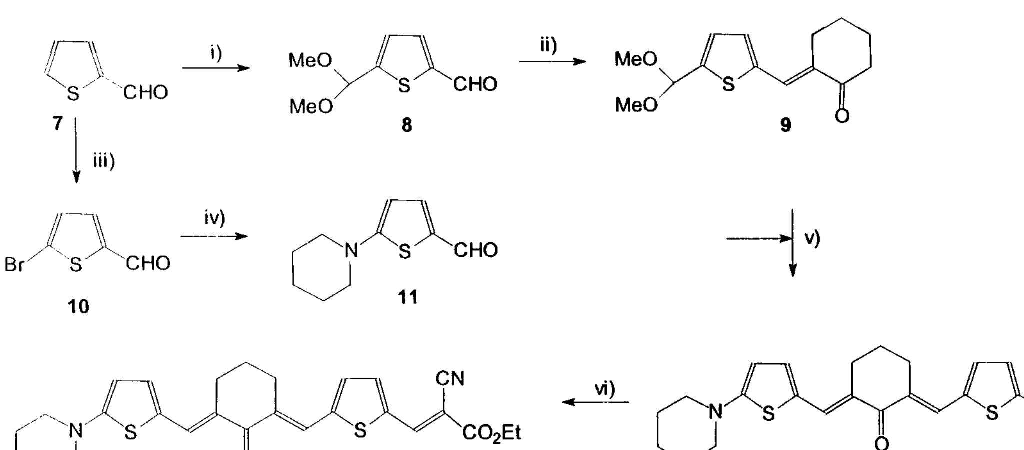
Scheme 2. Reaction sequences used for the synthesis of Pi-CO-CHO (**5a**), Pi-CO-CN (**6a**), and Pi-CO-Ba (**6b**). Reagents and conditions: i) $AlCl_3$, CH_2Cl_2; ii) piperidine, 120 °C, overnight; iii) a) LDA, THF, −40 °C, 30 min, b) DMF, rt, 90 min, c) HCl, H_2O; iv) ethanol, $CH_2CN(CO_2Et)$, piperidine, 60 °C; v) ethanol, barbituric acid, triethylamine.

polarizabilities. Accordingly, the peak value of β is not reached within the range of electric fields that are applied.

Experimental study:

Synthesis of carbonyl-spaced chromophores: In a previous paper,[23] we reported on the electro-optical properties of the keto-spaced ethyl (*E*)-2-cyano-3-[5-(5-piperidino-2-thienylcarbonyl)-2]-2-propenoate chromophore **6a** (Pi-CO-CN). This chromophore was obtained by the synthetic pathway described in Scheme 2. The parent chromophores described in the present study were obtained by a related procedure with 5-(5-piperidino-2-thienylcarbonyl)-2-thiophenecarbaldehyde **5a** (Pi-CO-CHO) as the key intermediate. A Knoevenagel condensation of **5a** with ethyl cyanoacetate led to **6a** (Pi-CO-CN), while the condensation of the *N,N*-dimethyl barbituric acid led to the parent chromophore 1,3-dimethyl-5-[5-(5-piperidino-2-thienylcarbonyl)-2-thienylmethylene]hexahydro-2,4,6-pyrimidinetrione **6b** (Pi-CO-Ba) under the same conditions. The synthesis of the elongated chromophore **13** (Pi-CHex-CN), based on a cyclohexanone central spacer, required a different reaction pathway (Scheme 3). 2-Thiophenecarboxaldehyde (**7**) was easily transformed to 5-dimethoxymethyl-2-thiophene carboxaldehyde (**8**) by protection of the aldehyde group and further formylation with the *n*BuLi/DMF sequence, as reported previously.[24] This aldehyde **8** was then condensed onto cyclohexanone by the reaction described by Tsukerman and al.[25] to yield 2-{(*E*)-1-[(5-dimethoxymethyl)-2-thienyl]methylidene}-1-cyclohexanone (**9**). 5-Piperidino-2-thiophenecarboxaldehyde (**11**), which is readily obtained by the reaction of 5-bromo-2-thiophenecarboxaldehyde (**10**) with piperidine in the presence of triethylamine,[26] was then condensed with the cyclohexanone derivative **9** to yield 5-{2-oxo-3-[(*E*)-1-(5-piperidino-2-thienyl)methylidene]cyclohexylidenemethyl}-2-thiophenecarboxaldehyde (**12**) after deprotection of the aldehyde group under acidic conditions. A final Knoevenagel condensation of **12** with ethyl cyanoacetate led to **13** (Pi-CHx-CN).

Solvent effect on the linear and nonlinear optical properties of Pi-CO-CN: In any solution, the solute molecules are located



Scheme 3. Reaction sequences used for the synthesis of Pi-CHx-CN (**13**). Reagents and conditions: i) LDA, THF, DMF; ii) cyclohexanone, NaOH, H_2O; iii) Br_2, $CHCl_3$; iv) piperidine, triethylamine, toluene; v) NaOH, H_2O; vi) ethanol, $CH_2CN(CO_2Et)$, piperidine, 60 °C.

in the reaction field of the solvent. This field basically acts on the solute in the same way as an external electric field, that is, it is capable of modifying the ground-state polarization of the solutes, thus causing a shift of the optical band and a change in the transition moment.[21, 27] The accurate determination of the mean reaction field is difficult since it depends on the nature and arrangement of the surrounding solvent molecules. In the elegant approximation of Onsager,[28] the reaction field is directly related to the dielectric constant of the solvating medium.

In the present study, we decided to use a mixture of two solvents in different ratios in order to control the dielectric constant of the solvating medium in a continuous manner. Toluene and dimethylsulfoxide (DMSO) were selected for: i) their very different dielectric constants ($\varepsilon_{\text{toluene}} = 2.38$; $\varepsilon_{\text{DMSO}} = 46.45$), ii) their almost equal refraction indices ($n_{\text{toluene}} = 1.4969$; $n_{\text{DMSO}} = 1.4793$)—this feature provides an additional advantage: the use of Lorentz local field correction factors can be avoided, iii) their high miscibility, and iv) the high solubility of the chromophore in their mixtures. The large difference in their dielectric constants allows a continuous variation of ε over a wide range. Figure 4 depicts the evolution of the dielectric constant and the DMSO:toluene ratio.

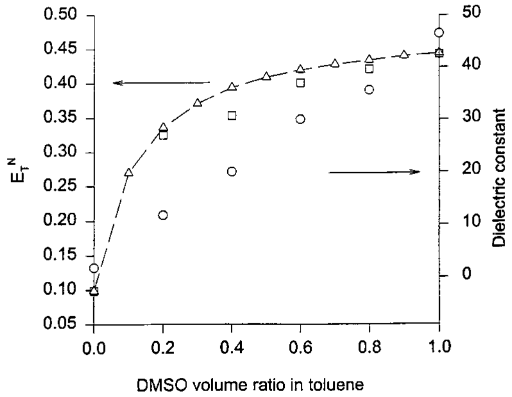


Figure 4. Evolution of the dielectric constant ε (○, as measured by a capacitance technique) and the E_T^N polarity scale (□ = experimental, △ = theoretical[30]) versus the DMSO volume ratio in the mixture of toluene/DMSO.

The dielectric constant, determined experimentally by a capacitance technique, was found to vary linearly with the DMSO content, as has already been described by McRae in the case of diethyl ether and acetonitrile mixtures.[29] The electrostatic model for the description of the solvation phenomena based on the dielectric constant considers the solvent as a macroscopic nonstructured continuum. However, specific solute/solvent interactions can take place on a molecular level within a structured discontinuum which consists of individual solvent molecules organized around the dipolar solute. A useful solvent polarity scale, based on a negative solvatochromic pyridinium N-phenolate betaine dye, is able to account for solute–solvent interactions[30] on a microscopic level, in contrast to the physical parameter ε. The evolution of the corresponding E_T^N scale with DMSO content is also depicted in Figure 4. The E_T^N values were determined experimentally by a UV/Vis analysis of Reichardt's dye.[30] A strong preferential solvation of the betaine dye by the more polar DMSO solvent can be deduced from the sharp effect of DMSO on the E_T^N values, even at very low volume ratio. This phenomenon has already been described by Bosch and Rosés in binary solvent mixtures.[31] Figure 4 also represents the fitted curve of the E_T^N-polarity scale by means of the model developed by Bosch and Rosés,[31] in which the preferential solvation parameters of the benzene–DMSO mixture instead of the toluene–DMSO mixture are used. The following discussion and figures will refer mostly to the ε-polarity scale, which is linearly related to the DMSO content.

The evolution of the lowest transition energy versus the dielectric constant, ε, of the binary mixture is indicative of the influence of the electric field on the charge transfer between the piperidino donor and the vinyl cyanoacetate acceptor in Pi-CO-CN. The solvatochromic behavior of Pi-CO-CN is shown in Figure 5. A substantial red shift or positive solvatochromism of 23 nm (0.14 eV) is observed as the solvent polarity is increased from pure toluene to pure DMSO. This is consistent with an increase in the dipole moment from the ground to the excited state. This red shift is even more pronounced when the solvent is changed from cyclohexane ($\varepsilon = 2.02$) to DMSO, a difference of $\lambda = 35$ nm (0.22 eV) between the lowest energy excitation values then measured. The UV/Vis spectra of Pi-CO-CN in the three pure solvents are displayed in Figure 5b. Two charge-transfer bands are present in the visible region of the spectrum; the second band, located around $\lambda = 350$ nm, is also influenced by the solvent polarity since a red shift of 21 nm (0.21 eV) occurs on changing from cyclohexane to DMSO.

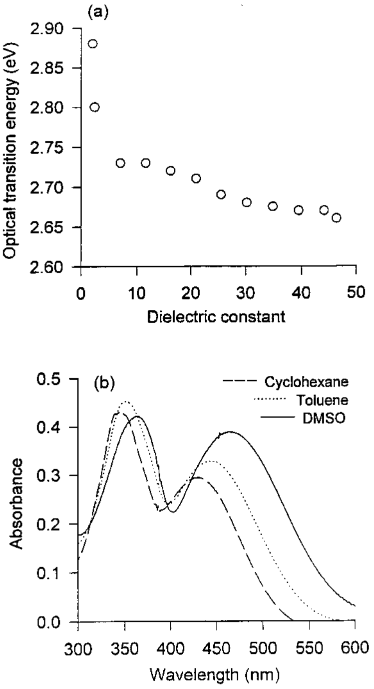


Figure 5. a) Evolution of the energy of the lowest optical band peak of Pi-CO-CN versus the polarity of the solvent; b) absorption spectra of Pi-CO-CN in cyclohexane, toluene, and DMSO.

The evolution of the (resonant) second-order polarizability for Pi-CO-CN as a function of the dielectric constant was measured by HRS at a fundamental wavelength of $\lambda = 1064$ nm. The β value of *p*-nitroaniline (PNA) in DMSO ($\beta = 29 \times 10^{-30}$ esu) was used as an external reference. All the values were corrected for the difference in the refractive indices by means of the local field factors. No multiphoton-induced fluorescence could be observed. The results are shown in Figure 6. After a small decrease in the β_{HRS} value between $\varepsilon = 2.3$ and 15, we observe a large peak with a maximum value of 600×10^{-30} esu for a dielectric constant of 40. The β value in pure DMSO ($\varepsilon = 46$) corresponds approximately to the initial and minimum value in toluene. We did not try to evaluate the static hyperpolarizability by means of the two-state model,[32] since it is clear from Figure 5 that two charge transfer transitions are present in the visible region of the spectrum; the two-state model might thus break down. We have observed the same absorption intensities at the resonant wavelength of 532 nm (corresponding to a half of the incident wavelength (1064 nm) for two toluene/DMSO ratios: 0/100 and 20/80; this suggests that the significant difference in the β values between the two solutions ($257 \pm 13 \times 10^{-30}$ esu and $611 \pm 31 \times 10^{-30}$ esu, respectively) is not simply due to a resonance phenomenon corresponding to the absorption of the second harmonic of the laser beam (provided that the lifetimes in the excited states are similar).

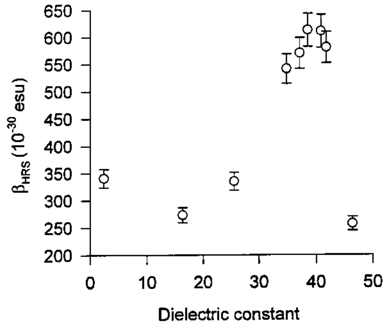
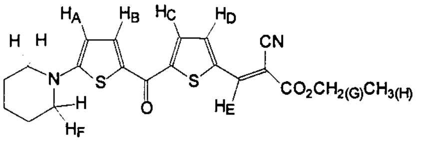


Figure 6. Evolution with solvent polarity of the experimental HRS β of Pi-CO-CN (fundamental wavelength $\lambda = 1064$ nm).

Solvent effect on ^{1}H NMR spectra of Pi-CO-CN: Another way to investigate the solvent effect on the geometric and electronic structure of model chromophores is to study the evolution of the ^{1}H NMR spectra with solvent polarity, as has been investigated previously by several groups.[33–38] Laszlo et al. focused on the effect of the solvent on the ^{1}H chemical shifts of several organic compounds,[33] while B. Nagy et al. modeled specific solvation phenomena[34] by means of NMR spectroscopy. More recently, ^{1}H NMR studies on merocyanine dyes have evidenced the proton shift induced by the solvent;[35–38] from the J_3 (^{1}H NMR) coupling constants of the olefinic protons, it was shown that simple merocyanine dyes exhibit a polyene-like structure in nonpolar solvents and a more zwitterionic structure in polar solvents.

In order to analyze the solvent effect on the electronic structure of the carbonyl-spaced chromophores, ^{1}H NMR spectra of 1 wt% solutions of ethyl (*E*)-2-cyano-3[5-(5-piperidino-2-thienylcarbonyl)-2]-2-propenoate Pi-CO-CN in [D$_8$]toluene/[D$_6$]DMSO mixtures were studied. Table 2 lists the ^{1}H chemical shifts of this chromophore as a function of the solvent polarity and the corresponding E_T^N values. The assignment of the chemical shifts in the aromatic region was checked by ^{1}H–^{1}H COSY experiments. It is also important to note that the chemical shift of tetramethylsilane (TMS), used as the internal reference for toluene/DMSO mixtures, is hardly influenced by the solvent polarity, as described in the Experimental Section. Although one cannot expect any simple relationship between chemical shift and π-electron densities in this type of complex molecules, a general trend can be deduced. The very sharp increase in chemical shift of the thiophene protons (A, B, C, D) and the methylene protons E, F, G at a low [D$_6$]DMSO content is indicative of a preferential solvation of the Pi-CO-CN solute by the more polar DMSO solvent molecules (see labeling in Table 2). A rather strong acid–base interaction between DMSO (or more likely its charged mesomeric form, $Me_2S^+-O^-$) and the (partly) positively charged amino nitrogen in the delocalized quinoid **B** and **C** forms of Scheme 1 can be expected to occur. Actually, the linear relationship observed between the proton shifts and the E_T^N-polarity scale (Figure 7) is consistent with the presence of such specific solvation phenomena. The occurrence of a solvent polarity-induced evolution from a neutral aromatic structure to a zwitterionic quinoid structure can be also deduced from an analysis of chemical shifts and J_3 coupling constants. A net downfield solvent-induced chemical shift of up to 0.56 ppm for the nonconjugated methylene F

Table 2. Chemical shifts and coupling constants for Pi-CO-CN in CDCl$_3$, [D$_8$]toluene, [D$_6$]DMSO, and a 50/50 mixture of [D$_8$]toluene/[D$_6$]DMSO.



Solvent	δA	δB	J(H$_A$,H$_B$) [Hz]	δC	δD	J(H$_C$,H$_D$) [Hz]	δE	δF	δG	δH	ε	E_T^N
CDCl$_3$	6.08	7.73	4.8	7.73	7.87	4.0	8.30	3.40	4.39	1.39	4.67	0.259
[D$_8$]toluene	5.60	7.58	4.5	7.38	7.23	4.0	7.93	2.75	3.94	1.00	1.81	0.099
[D$_8$]toluene/[D$_6$]DMSO (50/50)	6.22	7.84	4.6	7.83	8.00	4.0	8.58	3.23	4.23	1.24	20.05	0.385
[D$_6$]DMSO	6.37	7.89	4.8	7.98	8.09	4.0	8.64	3.31	4.32	1.31	46.45	0.444
Δ(toluene/DMSO)	– 0.75	– 0.31		– 0.6	– 0.78		– 0.7	– 0.56	– 0.38	– 0.31		

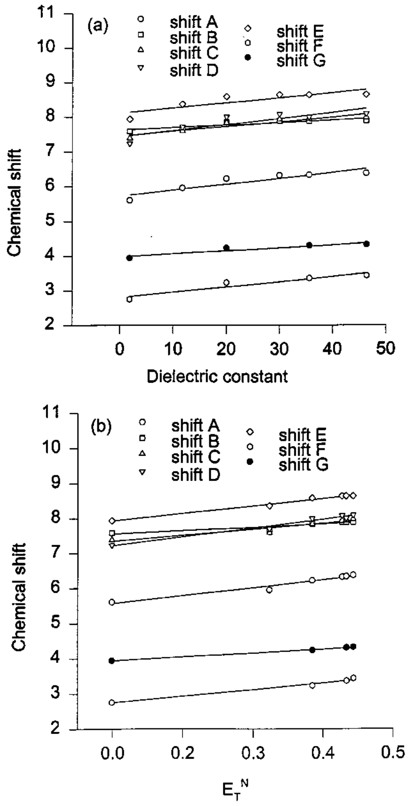


Figure 7. Evolution of the ^1H chemical shifts in Pi-CO-CN with respect to: a) the dielectric constant and b) the E_T^N polarity scale (see labeling in Table 2).

protons attached to the *N*-piperidino donor group is observed on changing from pure toluene to pure DMSO (see Table 2). This can be attributed to the electron deficiency on these protons due to the positive charge induced on the amino nitrogen in the delocalized quinoid **B** and **C** forms (Scheme 1). This solvent effect is significantly larger than that induced by the polar solvent on the nonconjugated methylene G and H protons. The very low chemical shift induced by the solvent on proton B, compared to adjacent protons A, C, and D, is also indicative of a net increase in electron density on this position in the delocalized quinoid **B** and **C** forms. A slight increase in the $J(H_A,H_B)$ coupling constant in the donor segment of the chromophore [$J(H_A,H_B) = 4.5$ Hz (pure toluene) to 4.8 Hz (pure DMSO)] can be related to an increase in π-conjugation between carbons bearing these A and B protons in the quinoid form, which is in agreement with the results of the calculations. This solvent-induced variation in the $J(H_A,H_B)$ coupling constant is, however, lower than in polymethine dyes,[36] probably because of the aromatic character of the thiophene ring. The analysis of $J(H_C,H_D)$ coupling constants in the acceptor thiophene leads to the conclusion that the electronic structure in the acceptor segment is less affected by the increase in polarity.

Influence of the electron-acceptor strength: The solvent effects on the optical spectra and molecular (hyper)polarizabilities of Pi-CO-CHO and Pi-CO-Ba have been studied and compared to those of Pi-CO-CN. On the scale of acceptor strength, the aldehyde group is the weakest of the three while the barbituric group is known to be one of the strongest acceptor groups, the vinyl cyanoacetate group in Pi-CO-CN is of intermediate strength. Substitution of the vinyl cyanoacetate group by the aldehyde group leads to a significant blue shift of the lowest transition energy; moreover, only one transition is observable in the visible part of the Pi-CO-CHO spectrum. Solvatochromic analysis of the latter shows a red shift of ≈19 nm (0.13 eV) on changing from toluene to DMSO and 30 nm (0.21 eV) for the change from cyclohexane to DMSO (Figure 8a). On the other hand, increasing the strength of the acceptor by substituting the vinyl cyanoacetate group by the barbituric acid terminal group induces a rather complex solvatochromic behavior, as illustrated in Figure 8b; the increase in the solvent polarity from cyclohexane to toluene induces a red shift while a higher solvent polarity leads to a blue shift of the lowest transition and a red shift of the second transition; in pure DMSO, the two transitions are no longer distinguishable.

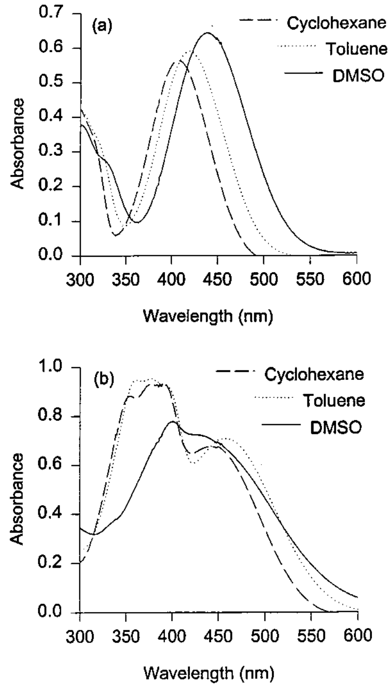


Figure 8. Absorption spectra of: a) Pi-CO-CHO and b) Pi-CO-Ba in cyclohexane, toluene, and DMSO.

Figure 9a represents the evolution of the second-order polarizability β for the Pi-CO-CHO chromophore as a function of the dielectric constant of the binary mixture toluene/DMSO. No significant variation of the resonant hyperpolarizability is observed when the polarity is progressively increased from $\varepsilon = 2.38$ to $\varepsilon = 46.45$. The small fluctuations observed are in the range of experimental error.

More interesting is Figure 9b, which describes the evolution of β for the Pi-CO-Ba chromophore. A peak in the resonant hyperpolarizability is observed for $\varepsilon = 32$, which corresponds to a maximum value of 1000×10^{-30} esu. Because of the presence of two charge-transfer transitions, the static hyperpolarizability has not been evaluated by the two-level

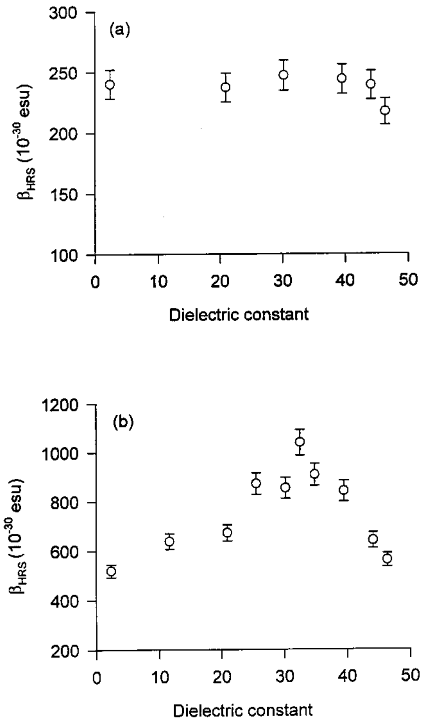


Figure 9. Evolution of the experimental HRS β of: a) Pi-CO-CHO and b) Pi-CO-Ba with solvent polarity (fundamental wavelength $\lambda = 1064$ nm).

model.[32] As expected, a comparison between the β curves for chromophores Pi-CO-CHO (Figure 9a), Pi-CO-CN (Figure 6), and Pi-CO-Ba (Figure 9b) indicates that a higher solvent polarity or dielectric constant is needed in order to reach the maximum value of β for a weaker acceptor strength; in the case of the weakest acceptor strength (Pi-CO-CHO), no peak is actually reached (a higher polarity than that of DMSO appears to be necessary, but still might not be sufficient in order to observe a maximum).

Effect of the π-conjugated path length: The chromophore Pi-CHex-CN (see Figure 1b) is composed of a piperidino donor group and a vinyl cyanoacetate acceptor group connected through a 2-(2-thienylidene)cyclohexanone semiconjugated spacer; it is thus longer than Pi-CO-CN by two double bonds. The UV/Vis spectra of Pi-CHex-CN in cyclohexane, toluene, and DMSO are given in Figure 10a. As was the case for Pi-CO-Ba, no clear absorption maximum can be determined and several transitions are present in the visible part of the spectrum. Although no significant red shift is observed on changing the solvent from cyclohexane to toluene, a sharp positive solvatochromism of ≈30 nm of the lowest transition is measured on changing to the more polar DMSO. The molecular hyperpolarizability values determined by HRS (at $\lambda = 1064$ nm) are displayed in Figure 10b. The maximum of β is located here around a dielectric constant $\varepsilon = 26$ corresponding to a 50/50 (v/v) toluene/DMSO mixture. The position of the peak is shifted to a lower polarity compared to Pi-CO-CN, which is consistent with the fact that a longer conjugated path reduces the electric field required to observe the maximum of β.[26]

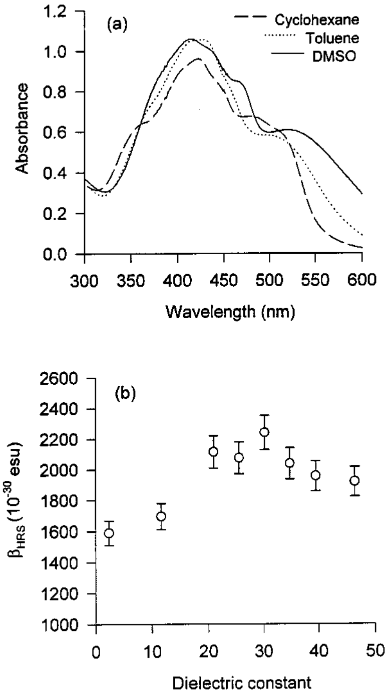


Figure 10. a) Absorption spectra of Pi-CHex-CN in cyclohexane, toluene, and DMSO; b) evolution of the experimental HRS β of Pi-CHex-CN with solvent polarity (fundamental wavelength $\lambda = 1064$ nm).

Comparison of theory and experiment: General trends in the relationship between theoretical and experimental results can be deduced from the observations reported above. The experimental evolution of the energy of the first optical transition with respect to ε for Pi-CO-CN (Figure 5a) has been compared to the corresponding theoretical quantity, that is, the evolution of the transition energy between the ground state and the first excited state versus ***F*** for DM-CO-CHO. An overall decrease of 3 eV is determined theoretically for DM-CO-NO_2 for static fields going from 0 to 10^8 V cm^{-1}. Experimentally, changing the solvent from cyclohexane ($\varepsilon = 2.02$) to toluene ($\varepsilon = 2.38$) induces a bathochromic shift of 0.1 eV, which confirms a very rapid decrease of the first transition energy at low solvent polarities. However, a very small variation of 0.14 eV is observed when ε changes from 2.38 (toluene) to 46 (DMSO). The reason for this slow evolution is probably related to a preferential solvation phenomenon of the dipolar chromophore by the more polar solvent that occurs as the content of DMSO increases in the toluene/DMSO binary mixture. This preferential solvation phenomenon induces an inhomogeneous electric reaction field around the chromophore in solution and the theoretical and experimental transitions cannot be compared in any simple way.

A large influence of the electric field or reaction field in solution on the electronic cloud in the donor segment of the chromophore has been deduced from both theory and experiment. The neutral and zwitterionic forms described in Scheme 1 participate in the actual structure of chromophores, as shown by the theoretical analysis of the π-BOs on DM-CO-NO_2 and the ^{1}H NMR data in the case of Pi-CO-CN. Note that a similar participation of the neutral and zwitterionic structures as the solvent polarity was increased has been reported by Kessler and Wolfbeis[13] in related keto-spaced chromophores.

An interesting parallel can be made in terms of the molecular hyperpolarizabilities. The evolution of the calculated hyperpolarizability β_{HRS} versus $\boldsymbol{F}$ for DM-CO-NO_2 can be compared qualitatively with the evolution of the resonant experimental second-order polarizability (at $\lambda = 1064$ nm) versus ε. They both present a maximum, the former at an electric field of 6.7×10^7 V cm^{-1} and the latter at $\varepsilon \approx 40$. There is also a qualitative agreement between the theoretical β curve (Figure 3c) and the experimental β evolution (Figure 9a) for the aldehyde-substituted chromophores DM-CO-CHO and Pi-CO-CHO, respectively; no peak can be observed experimentally in the range of polarities of the toluene/DMSO mixtures and only a very small increase in β versus $\boldsymbol{F}$ is obtained theoretically.

To summarize, despite qualitatively parallel trends between the evolution of the experimental data as a function of ε and that of the theoretical results versus $\boldsymbol{F}$, there are major quantitative disagreements: i) the experimental evolution in transition energy is much smaller; for instance, in the case of Pi-CO-CN, as the value of ε is changed from 2.02 to the ε value leading to the β peak, the transition energy decreases by $\approx$0.25 eV. If we take into consideration Onsager's theory (since the evolution in the reaction field from $\varepsilon = 1$ to 2 is half that up to the largest ε values), this would mean a global evolution from the gas phase to $\varepsilon \approx 40$ of the order of 0.5 eV; the theoretical evolution is about 6 times as large. ii) The measured peak β value is only about twice as large as the β values measured at small ε; the corresponding calculated increase is over one order of magnitude. These discrepancies can be ascribed to the occurrence of specific interactions due to DMSO in solution, which have not been taken into account in the calculations.

Conclusions

The synthesis of novel carbonyl-spaced NLO chromophores has been carried out and the linear and nonlinear optical properties in solution have been determined. Semiempirical INDO/SDCI calculations of two related model compounds have been correlated with the experimental results. Qualitatively, a parallel is found between the dependence of the HRS second-order polarizability with respect to solvent polarity and the theoretical evolution of β as a function of the ground-state polarization, which was tuned by the application of a static homogeneous electric field. The quantitative discrepancies between the experimental data and the calculated transition energies and β values are attributed to a preferential solvation phenomenon that induces an inhomogeneous and very different reaction field around the dissolved chromophore. This work illustrates that a joint theoretical and experimental investigation can lead to a better perception of, on one hand, the influence of environmental factors on the polarizabilities and, on the other hand, the role of a carbonyl spacer in tuning the charge transfer along a push–pull-conjugated chromophore.

Experimental Section

General: 2-Thiophenecarboxaldehyde (Acros), trimethyl orthoformiate (Janssen), cyclohexanone (Baker), triethylamine (Janssen), piperidine (Janssen), lithium diisopropylamide (LDA; Aldrich, 2 M solution in heptane, THF, ethylbenzene), *N,N*-dimethylbarbituric acid (Fluka), and ethyl cyanoacetate (Fluka) were used as received. *N,N*-dimethylformamide (DMF) was dried and distilled over phosphorus pentoxide prior to use. Tetrahydrofuran (THF) was dried and distilled over sodium/benzophenone. Dimethylsulfoxide (DMSO; Merck) and toluene (JP Baker) for spectroscopic analyses were of analytical grades and used as received. [D_8]Toluene (Aldrich) and [D_6]DMSO (Aldrich) were used as received. The ^{1}H spectra were recorded on a Bruker AM 400 spectrometer; the chemical shifts in the experimental section are given relative to tetramethylsilane (TMS) and recorded in $CDCl_3$. *J* values are given in Hertz. Since some authors have reported a large solvent effect on the ^{1}H and ^{13}C chemical shifts of TMS,[33] mainly in aromatic solvents where diamagnetic anisotropy is important, the validity of TMS as the internal reference was checked by the use of cyclohexane as a second internal reference in the toluene/DMSO mixtures. The chemical shift of cyclohexane is known to be independent of solvent polarity;[39] its chemical shift in various toluene/DMSO mixtures was found to be constant ($\delta = 1.40$ relative to TMS). Therefore, all chemical shifts are expressed relative to TMS, $\delta = 0.0$. The IR spectra were recorded on a Perkin–Elmer 1600FT spectrometer. UV/Vis analyses were performed on a Hitachi U-3300 spectrometer with concentrations $\approx 5 \times 10^{-5}$ M. Hyper-Rayleigh scattering was performed at a fundamental wavelength of $\nu = 1064$ nm (Nd-YAG laser). The setup and conditions have been described elsewhere.[40]

Synthetic procedures: The synthesis of ethyl (*E*)-2-cyano-3-[5-(5-piperidino-2-thienylcarbonyl)-2]-2-propenoate (**6a**, Pi-CO-CN) and the intermediate compounds have been described elsewhere.[23]

Synthesis of 1,3-dimethyl-5-[5-(5-piperidino-2-thienylcarbonyl)-2-thienylmethylene]hexahydro-2,4,6-pyrimidinetrione (**6b**, Pi-CO-Ba): In a single-necked flask (50 mL), 5-(5-piperidino-2-thienylcarbonyl)-2-thiophenecarbaldehyde[23] (0.5 g, 0.001.6 mol) was dissolved in dry ethanol (40 mL). *N,N*-dimethyl barbituric acid (0.312 g, 0.002 mol) and 2 drops of piperidine were then added to the solution. The mixture was heated at 80 °C for 0.5 h and then allowed to cool to room temperature. The mixture was hydrolyzed with HCl (0.1 N, 5 mL) and the aqueous phase was extracted with $CHCl_3$ (2×50 mL). The organic phases were washed thoroughly with HCl (0.1 N) and water and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure and the red solid purified by chromatography (silica gel; *n*-hexane/ethyl acetate (1:1, *v*/*v*)) to give **6b**. Yield: 0.4 g (56 %); ^{1}H NMR ($CDCl_3$): $\delta = 8.69$ (s, 1 H), 7.80 (d, $J = 4.0$ Hz, 1 H), 7.73–7.71 (m, 2 H,), 6.09 (d, $J = 4.4$ Hz, 1 H), 3.37 (s, 6 H), 3.35 (t, 4 H, *J*), 1.75–1.60 (m, 6 H); IR (KBr): 2935, 2853, 1688, 1570, 1474, 1440, 1379, 1322, 1238, 1124, 1087, 788, 753, 725 cm^{-1}.

Synthesis of 2-{(*E*)-1-[(5-dimethoxymethyl)-2-thienyl]methylidene}-1-cyclohexanone (**9**): In a 250 mL flask, 5-dimethoxymethyl-2-thiophene carboxaldehyde (**8**, 1.29 g, 0.0069 mol) was dissolved in cyclohexanone (5 mL) and water (100 mL). A solution of sodium hydroxide (0.27 g, 0.0069 mol) in water (5 mL) was added dropwise and the reaction mixture was stirred overnight. The crude mixture was then extracted with diethyl ether (2×50 mL) and the organic phases washed successively with sodium bicarbonate and water and then dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the yellow oil obtained was purified by silica gel chromatography (*n*-hexane/ethyl acetate (1:1, *v*/*v*)) to give **9**. Yield: 1.56 g (85 %); ^{1}H NMR ($CDCl_3$): $\delta = 7.77$ (d, $J = 2.0$ Hz, 1 H), 7.25 (d, $J = 3{,}6$ Hz, 1 H), 7.09 (d, $J = 3{,}6$ Hz, 1 H), 5.66 (s, 1 H), 3.35 (s, 6 H), 2.83 (m, 2 H) 2.51 (t, 2 H, $J = 6.0$), 1.88 (m, 4 H); IR (neat): 2936, 2828, 1710, 1673, 1578, 1348, 1317, 1250, 1193, 1142, 1084, 1063, 974, 818, 789 cm^{-1}.

Synthesis of 5-piperidino-2-thiophenecarboxaldehyde (**11**): In a 250 mL flask equipped with a condenser and under a nitrogen atmosphere, 2-bromo-5-thiophene carboxaldehyde (**10**, 8.4 g, 0.051 mol), triethylamine (3.7 mL, 0.051 mol), and piperidine (4.36 g, 0.051 mol) were dissolved in dry toluene (100 mL) and refluxed at 120 °C over a period of 3 days. The reaction mixture was then hydrolyzed with HCl (0.1 N, 5 mL) and washed vigorously with HCl (0.1 N), $NaHCO_3$, and H_2O. The organic phase was dried over $MgSO_4$, the solvent removed under reduced pressure, and the brown solid obtained was purified by silica gel chromatography (*n*-hexane/

ethyl acetate (8:2, *v*/*v*)) to give **11**. Yield 4.28 g (50%); ^{1}H NMR (CDCl$_3$): $\delta = 9.50$ (s, 1H), 7.47 (d, $J = 4.5$ Hz, 1H), 6.06 (d, $J = 4.5$ Hz, 1H), 3.34 (t, $J = 4.4$ Hz, 4H), 1.69 (m, 6H); IR (KBr): 2974, 2882, 1672, 1596, 1440, 1415, 1333, 1054, 963, 792 cm^{-1}.

Synthesis of 5-{2-oxo-3-[(*E*)-1-(5-piperidino-2-thienyl)methylidene]cyclohexylidenemethyl}-2-thiophenecarboxaldehyde (**12**): In a 50 mL flask equipped with a condenser, 5-piperidino-2-thiophenecarboxaldehyde (**11**, 0.5 g, 0.0026 mol) and 2-{(*E*)-1-[(5-dimethoxymethyl)-2-thienyl]methylidene}-1-cyclohexanone (**9**, 0.7 g, 0.0026 mol) were dissolved in ethanol (20 mL). A solution of sodium hydroxide (0.104 g, 0.0026 mol) in water (5 mL), was slowly added to the reaction mixture, which was then heated at 100 °C over a period of 4 days. Subsequently, the reaction mixture was hydrolyzed with HCl (0.1N, 5 mL) and extracted twice with CHCl$_3$. The organic phases were washed with HCl (0.1N) and NaHCO$_3$ and dried over MgSO$_4$, and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate (1:1, *v*/*v*)) to give **12**. Yield: 0.25 g (28%); ^{1}H NMR (CDCl$_3$): $\delta = 9.83$ (s, 1H), 7.93 (m, 1H), 7.89 (m, 1H), 7.74 (d, $J = 4.0$ Hz, 1H), 7.36 (d, $J = 4.0$ Hz, 1H), 7.19 (d, $J = 4.3$ Hz, 1H), 6.10 (d, $J = 4.3$ Hz, 1H), 3.30 (t, $J = 5.0$ Hz, 4H), 2.93 (t, $J = 4.0$ Hz, 2H), 2.86 (t, $J = 4.0$ Hz, 2H), 1.95 (m, 2H), 1.73 to 1.69 (m, 6H); IR (neat): 2937, 2854, 1622, 1537, 1497, 1445, 1381, 1247, 1065, 890, 858, 763, 754 cm^{-1}.

Synthesis of ethyl (*E*)-2-2-cyanomethyl-3-{5-2 oxo-3-[(*E*)-1-(5-piperidino-2-thienylmethylidene)cyclohexylidenemethyl]-2-thienyl}-2-propenoate (**13**, Pi-CHex-CN): Following the previously described procedure for the synthesis of **6a**, 5-{2-oxo-3-[(*E*)-1-(5-piperidino-2-thienyl)methylidene]cyclohexylidenemethyl}-2-thiophenecarboxaldehyde (**12**, 0.09 g, 0.00027 mol), and ethyl cyanoacetate (0.03 mL, 0.00027 mol) were dissolved in toluene (10 mL). After the addition of 2 drops of piperidine, the reaction mixture was heated overnight at 60 °C. The reaction mixture was then hydrolyzed with HCl (0.1 N, 2 mL) and extracted twice with CHCl$_3$. The organic phases were washed with HCl (0.1N) and NaHCO$_3$, dried over MgSO$_4$ and the solvent was removed under reduced pressure. The crude product was purified by silica gel chromatography (*n*-hexane/ethyl acetate (1:1, *v*/*v*)) to give **13**. Yield: 0.05 g (43%); ^{1}H NMR (CDCl$_3$): $\delta = 8.29$ (s, 1H), 7.93 (s, 1H), 7.75 (s, 1H), 7.76 (d, $J = 4.0$ Hz, 1H), 7.36 (d, $J = 4.0$ Hz, 1H), 7.20 (d, $J = 4.6$ Hz, 1H), 6.11 (d, $J = 4.3$ Hz, 1H), 4.39 (q, $J = 7{,}2$ Hz, 2H), 3.32 (t, $J = 4.6$ Hz, 4H), 2.96 and 2.85 (t, $J = 5{,}2$ Hz, 4H), 1.99 (t, $J = 6{,}2$ Hz, 2H), 1.70 (m, 6H) and 1.42 (t, $J = 7{,}2$ Hz, 3H); IR (KBr): 2934, 2855, 2216, 1715, 1644, 1583, 1514, 1470, 1432, 1375, 1271, 1240, 1197, 1166, 1142, 1067, 1016, 940, 887, 854, 810, 757 cm^{-1}.

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[1] a) Special issue on *Optical Nonlinearities in Chemistry*, *Chem. Rev.* **1994**, *94*; b) *Materials for Nonlinear Optics—Chemical Perpectives* (Eds.: S. R. Marder, J. E. Sohn, G. D. Stucky), *ACS Symp. Ser.* **1991**, *455*; c) *Nonlinear Optical Properties of Organic Molecules and Crystals* (Eds.: D. S. Chemla, J. Zyss), Academic Press, Orlando, **1987**.

[2] a) L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10631; b) L.-T. Cheng, W. Tam, S. H. Stevenson, G. R. Meredith, G. Rikken, S. R. Marder, *J. Phys. Chem.* **1991**, *95*, 10643.

[3] M. J. S. Dewar, A. J. Holder, *Heterocycles* **1989**, *28*, 1135.

[4] a) V. P. Rao, A. K.-Y. Jen, Y. Cai, *Chem. Commun.* **1996**, 1237; b) K. Y. Wong, A. K.-Y. Jen, V. P. Rao, K. Drost, R. M. Mininni, *Proc. SPIE* **1992**, *1775*, 74 and references therein.

[5] a) S. Gilmour, S. R. Marder, J. W. Perry, L.-T. Cheng, *Adv. Mater.* **1994**, *6*, 494; b) A. K.-Y. Jen, Y. Cai, P. V. Bedworth, S. R. Marder, *Adv. Mater.* **1997**, *9*, 132.

[6] M. Blenkle, P. Boldt, C. Bräuchle, W. Grahn, I. Ledoux, H. Nerenz, S. Stadler, J. Wichern, J. Zyss, *J. Chem. Soc. Perkin Trans. 2* **1996**, 1377.

[7] *Chem. Eng. News* **1996**, 4 March, 22.

[8] J. Zyss, in *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics* (Eds.: J. L. Brédas, R. R. Chance), *NATO ASI Ser.*, *Ser. E: Applied Sciences, Vol. 182*, **1990**, 451.

[9] a) G. Mignani, M. Barzoukas, J. Zyss, G. Soula, F. Balegroune, D. Grandjean, D. Josse, *Organometallics* **1991**, *10*, 3660; b) D. Hissink, P. F. Van Hutten, G. Hadziioannou, F. Van Bolhuis, *J. Organomet. Chem.* **1993**, *454*, 25.

[10] J.-X. Zhang, P. Dubois, R. Jérôme, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1209.

[11] T. Kogej, F. Meyers, S. R. Marder, R. Silbey, J. L. Brédas, *Synth. Met.* **1997**, *85*, 1141.

[12] T. Kogej, R. Silbey, S. R. Marder, J. L. Brédas, unpublished results.

[13] M. A. Kessler, O. S. Wolfbeis, *Spectrochim. Acta* **1991**, *47A*, 187.

[14] a) J. Kawamata, K. Inoue, H. Kasatani, H. Terauchi, *Jpn. J. Appl. Phys.* **1992**, *31*, 254; b) J. Kawamata, K. Inoue, T. Inabe, M. Kiguchi, M. Kato, Y. Taniguchi, *Chem. Phys. Lett.* **1996**, *249*, 29; c) Y. Kitaoka, T. Sasaki, S. Nakai, Y. Goto, *Appl. Phys. Lett.* **1991**, *59*, 19; d) Y. Goto, A. Hayashi, Y. Kimura, M. Nakayama, *J. Cryst. Growth* **1991**, *108*, 688.

[15] F. Meyers, S. R. Marder, B. M. Pierce, J. L. Brédas, *J. Am. Chem. Soc.* **1994**, *116*, 10703.

[16] J. A. Pople, D. L. Beveridge, P. A. Dobosh, *J. Chem. Phys.* **1967**, *47*, 2026.

[17] J. Ridley, M. C. Zerner, *Theor. Chim. Acta* **1973**, *32*, 11.

[18] a) *Solvents and Solvent Effects in Organic Chemistry* (Ed.: C. Reichardt) VCH, Weinheim, **1988**; b) C. J. F. Böttcher, *Theory of Electric Polarization: Dielectrics in Static Fields*, Elsevier, Amsterdam, **1973**, 135; c) A. Willetts, J. E. Rice, D. M. Burland, D. P. Shelton, *J. Chem. Phys.* **1992**, *97*, 7590.

[19] B. J. Orr, J. F. Ward, *Mol. Phys.* **1971**, *20*, 513.

[20] I. D. L. Albert, T. J. Marks, M. A. Ratner, *J. Phys. Chem.* **1996**, *100*, 9714.

[21] S. R. Marder, C. B. Gorman, F. Meyers, J. W. Perry, G. Bourhill, J. L. Brédas, B. M. Pierce, *Science* **1994**, *265*, 632.

[22] S. F. Cyvin, J. E. Rauch, J. C. Decius, *J. Chem. Phys.* **1965**, *43*, 4083.

[23] C. Maertens, C. Detrembleur, P. Dubois, R. Jérôme, P.-A. Blanche, P. Lemaire, *Chem. Mater.* **1998**, *10*, 1010.

[24] C. Maertens, J.-X. Zhang, P. Dubois, R. Jerôme, *J. Chem. Soc. Perkin Trans. 2* **1996**, 713.

[25] S. V. Tsukerman, L. A. Kutulya, V. F. Lavruskin, *Zh. Obs. Khim.* **1964**, *34*, 3597.

[26] I. Cabrera, O. Althoff, H.-T. Man, H. N. Yoon, *Adv. Mater.* **1994**, *6*, 43.

[27] a) W. Liptay, *Angew. Chem.* **1969**, *81*, 195; *Angew. Chem. Int. Ed. Engl.* **1969**, *8*, 177; b) C. N. R. Rao, S. Singh, V. P. Senthilnathan, *Chem. Soc. Rev.* **1976**, *5*, 297; c) M. Stähelin, D. M. Burland, J. E. Rice, *Chem. Phys. Lett.* **1992**.

[28] L. Onsager, *J. Am. Chem. Soc.* **1936**, *58*, 1486.

[29] E. McRae, *J. Phys. Chem.* **1957**, *61*, 562.

[30] The maximum of absorption of 10^{-5}M solutions of 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate or Reichardt's dye in DMSO/toluene mixtures were determined by UV/Vis analysis. The use of the formula $E_T^N = (28591/\lambda_{max}(\text{nm}) - 30.7)/32.4$ leads to the values of E_T^N given in Figure 4. For a review, see: C. Reichardt, *Chem. Rev.* **1994**, *94*, 2319.

[31] E. Bosch, M. Rosés, *J. Chem. Soc. Faraday Trans.* **1992**, *88,* 3541.

[32] J. F. Oudar, D. S. Chemla, *Chem. Phys.* **1977**, *66*, 2664; J. L. Oudar, *J. Chem. Phys.* **1977**, *67*, 446.

[33] E. Engler, P. Laszlo, *J. Am. Chem. Soc.* **1971**, *93*, 1318.

[34] O. B. Nagy, M. Wa Muanda, J. B. Nagy, *J. Chem. Soc. Faraday Trans. 1* **1978**, *74*, 2210.

[35] R. Radeglia, S. Dähne, *J. Mol. Structure* **1970**, *5*, 399.

[36] S. R. Marder, J. W. Perry, G. Bourhill, C. B. Gorman, B. G. Tiemann, K. Mansour, *Science* **1993**, *261*, 186.

[37] M. Blanchard-Desce, V. Alain, P. V. Bedworth, S. R. Marder, A. Fort, C. Runser, M. Barzoukas, S. Lebus, R. Wortmann, *Chem. Eur. J.* **1997**, *3*, 1091.

[38] J. O. Morley, R. M. Morley, R. Docherty, M. H. Charlton, *J. Am. Chem. Soc.* **1997**, *119*, 10192.

[39] D. Ziessow, M. Carroll, *Ber. Bunsenges.* **1972**, *76*, 61.

[40] See, for instance: E. Hendrickx, K. Clays, A. Persoons, C. Dehu, J. L. Brédas, *J. Am. Chem. Soc.* **1995**, *117*, 3547.

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