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Intramolecular charge transfer and enhanced quadratic optical non-linearities in push–pull polyenes

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Abstract

Push–pull polyenes, which have an electron-donating group (D) and an electron-withdrawing group (A) grafted on opposite ends of a conjugated polyenic chain, are of particular interest as model compounds for long-distance intramolecular charge transfer (ICT), as well as potent non-linear optical chromophores. Several series of push–pull polyenes of increasing length, combining aromatic donor moieties and various acceptor groups, have been prepared and studied. Their linear and non-linear optical properties have been investigated by performing electro-optical absorption measurements (EOAM) and electric-field-induced second-harmonic generation (EFISH) experiments in solution.

Each molecule shows a broad and intense ICT absorption band in the visible associated with an increase in the dipole moment ($\Delta\mu$). Lengthening the polyenic chain linking the D and A groups results in a bathochromic shift of the ICT absorption band and induces a linear increase in the excited state dipole. In contrast, the ground state dipole remains roughly constant. As a result, the longest molecules exhibit huge $\Delta\mu$ values (up to 42 D) as well as markedly enhanced quadratic hyperpolarizabilities (β). In addition, the nature of the end groups has been found to influence strongly both the ICT and optical non-linearities: larger β and $\Delta\mu$ values, as well as steeper length dependences, are obtained with push–pull phenylpolyenes bearing strong acceptors. © 1997 Elsevier Science S.A.

Keywords: Electric-field-induced second-harmonic generation (EFISH); Electro-optical absorption measurements (EOAM); Excited state dipoles; Hyperpolarizabilities; Intramolecular charge transfer; Non-linear optics; Push–pull polyenes

1. Introduction

In "push-pull" compounds, where an electron-donating group (D) and an electron-withdrawing group (A) interact via a π-conjugated system (with p-nitroaniline as the prototypical molecule), a partial intramolecular charge transfer (ICT) occurs from the donor moiety to the acceptor moiety through the conjugated path. This induces an asymmetric polarization of the ground state, which can lead to a significant ground state dipole. Such molecules are also characterized in solution by an intense absorption band in the UV-visible region. This ground to first excited state transition is usually assigned to ICT absorption which can either induce an enhancement or a decrease in the dipole moment. Significant photoinduced changes in the dipole moment ($\Delta\mu$) have been reported for several D–π–A molecules, such as push–pull benzenes [1], stilbenes [1], biaryls [1,2], diphenylpolyynes [3] and oligothiophenes [4].

Examination of the data reported in Ref. [1] suggests that increasing the donor or acceptor strength leads to an increase in the $\Delta\mu$ values for push–pull benzenes, styrenes, biphenyls and stilbenes. Such a trend is also noted for push–pull bithiophenes [4]. However, this is not the case for push–pull tolanes (i.e. donor–acceptor diphenylacetylenes) as observed from the data reported in Ref. [3].

Comparison of the $\Delta\mu$ values reported in Ref. [1] for homologous push–pull benzenes, biphenyls, styrenes and stilbenes demonstrates that lengthening the π-conjugated system connecting the D and A groups can result in significant increases in the photoinduced change in the dipole. Likewise, a pronounced enhancement of the $\Delta\mu$ values was noted for a series of push–pull carotenoids of increasing length [5].

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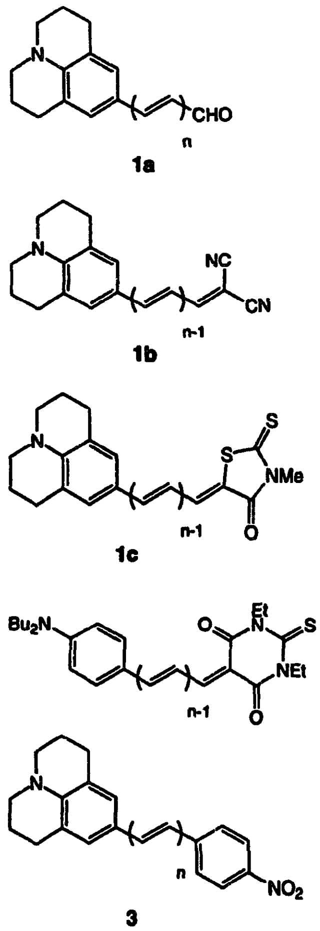
This is also the case for push-pull oligothiophenes which show an almost linear dependence of $\Delta\mu$ on the number of thiophene units, as indicated by examination of the $\Delta\mu$ values reported in Ref. [4]. In contrast, both experimental work and calculations have indicated a decrease in $\Delta\mu$ with increasing length for a series of push-pull diphenylpolyynes [3,6]. Both the length dependence and the magnitude of the $\Delta\mu$ values appear to depend on the nature of the π-conjugated system linking the D and A groups. For instance, examination of the semi-empirical calculations carried out on a series of push-pull polyenes reported in Ref. [7] reveals an increase in $\Delta\mu$ with increasing length, with a saturation for twelve conjugated double bonds. In contrast, homologous push-pull oligophenyls show a maximum for three phenyl units.

We have chosen to focus on a series of push-pull polyenes of increasing length since a recent experimental study emphasized the particular efficiency of the polyenic chain for achieving long-distance photoinduced ICT [5]. Further "molecular engineering" of the push-pull structure is needed in order to maximize the $\Delta\mu$ values for a given chain length. In particular, the nature of the D and A groups is expected to control the extent of the photoinduced change in the dipole (i.e. the magnitude of $\Delta\mu$) and may influence the length behaviour. Within this framework, we have investigated several series of push-pull polyenes of increasing length (Scheme 1). They have aromatic electron-donating end groups (i.e. the julolidine or dibutylaniline moiety) and bear various electron-withdrawing end groups. We have studied phenylpolyenes with acyclic (series **1a** and **1b**) or heterocyclic (series **1c** and **2**) acceptors. In addition, we have investigated a series of diphenylpolyenes with donor/acceptor terminal substituents (series **3**).

In order to characterize the photoinduced ICT phenomenon, we have studied the absorption properties by examining the solvatochromic behaviour and performing electro-optical absorption measurements (EOAM) in solution [1,8]. Likewise, we have investigated the quadratic optical non-linearities by performing electric-field-induced second-harmonic generation (EFISH) experiments in solution [9-11]. Push-pull compounds are of particular interest in terms of quadratic non-linear optical effects (such as second-harmonic generation or electro-optical modulation). Such molecules can display a large molecular quadratic non-linearity (i.e. quadratic hyperpolarizability β). The quantum two-level model relates this behaviour to the ICT phenomenon and predicts enhanced quadratic optical responses for push-pull compounds displaying low-lying and high oscillatory strength ICT transitions associated with a large photoinduced change in the dipole [12,13]. In the two-level approximation, the magnitude of the static quadratic hyperpolarizability $\beta(0)$ can be related to the ICT transition characteristics according to

$$\beta(0) = \frac{3\mu_{ge}^2 \Delta\mu}{2E_{ge}^2} \qquad (1)$$

where μ_{ge} and E_{ge} are the ICT transition dipole and energy respectively.



Scheme 1.

Of the various push-pull systems, the superiority of the polyenic system in terms of the quadratic hyperpolarizability β has been demonstrated [14]. A number of recent experimental studies have yielded pronounced increases in β with increasing polyenic length [14-23], the chain length behaviour depending markedly on the nature of the D and A end groups [14].

2. Experimental details

Push-pull phenylpolyenes of series **1** and **2** were prepared from phenylpolyenals bearing the donor moiety by Knoevenagel condensation which allowed for the grafting of the acceptor end groups [24,25]. Push-pull diphenylpolyenes of series **3** were synthesized by Wittig condensation of a phosphonium salt having the donor group with polyenals bearing the acceptor moiety [25]. Thus the synthetic strategy is based on the preparation of phenylpolyenals of increasing length functionalized with either donor or acceptor substituents. These conjugated polyenals were obtained from the generic aldehydes via sequential Wittig oxyprenylation followed by acidic hydrolysis [24-26]. All molecules were obtained as all-trans compounds (as shown by proton nuclear magnetic resonance (^{1}H NMR) studies) after chromatography followed by (re)crystallization. They were satisfactorily characterized by elemental analysis and mass spectroscopy.

Electronic absorption spectra were recorded with a Beckmann DU 600 or a Perkin–Elmer 340 spectrophotometer. The solvatochromic behaviour was investigated using spectroscopic grade solvents. The molar decadic extinction coefficients κ were obtained according to the Lambert–Beer equation. The transition dipoles μ_{ge} were determined by numerical integration of the absorption band as defined in Refs. [27,28].

The electro-optical absorption device has been described in Ref. [29]. EOAM involve studying the effect of an external electric field E_0 on the absorption of linearly polarized light by a dilute solution of a chromophore [1]. The EOA spectrum is given by

$$L\kappa/\sigma=\frac{(\kappa^E/\sigma)-(\kappa/\sigma)}{E_0^2} \qquad (2)$$

where σ is the wavenumber of the optical field and κ^E is the extinction coefficient of the solute in the presence of the applied field E_0. EOAM were performed at $T=298$ K in dioxan carefully purified and dried by column chromatography on basic alumina followed by distillation over sodium/potassium alloy under argon. The experimental error is in the range 1%–5%.

EFISH measurements were conducted with a Q-switched Nd^{3+}:YAG laser emitting pulses of about 8 ns duration at 1.064 μm. This emission was shifted to 1.907 μm by a hydrogen Raman cell at 40 bar. The experiments were performed using, for each molecule, solutions of increasing concentration in chloroform [10,11]. The measurements were calibrated relative to a quartz wedge. For the quartz reference, the experimental value of the quadratic susceptibility $d_{11}=1.2\times10^{-19}$ esu, determined at 1.06 μm, was used. To account for dispersion, this value was extrapolated to $d_{11}=1.1\times10^{-19}$ esu at 1.91 μm. The cubic contribution to the EFISH signal was neglected. The experimental accuracy is 10%.

3. Results

3.1. Absorption

The absorption spectra of the push–pull polyenes investigated in this work display an intense band in the visible. In each series of homologous compounds, a bathochromic shift, as well as a broadening of the low-energy absorption band, is observed with increasing polyenic chain length as shown in Fig. 1 for push–pull diphenylpolyenes of series 3.

For all molecules investigated in this work, the absorption maxima are red shifted with increasing solvent polarity. Such positive solvatochromism is characteristic of ICT transitions with an increase in the dipole moment on excitation [30]. The photoinduced change in the dipole (i.e. $\Delta\mu$ value) can be derived from the solvatochromic behaviour by using the quantitative treatment of solvatochromism proposed by a number of workers [27,28,31–33]. Most treatments are based on the Onsager model [34] according to which the "dissolved" molecule occupies a spherical cavity of radius a in the solvent which is viewed, in a simple approximation, as a continuum with dielectric constant ϵ_r. Polar solutes orientate and/or polarize the surrounding solvent molecules. As a result, the solvent medium generates an electric reaction field F across the solute molecule which can be expressed by [35]

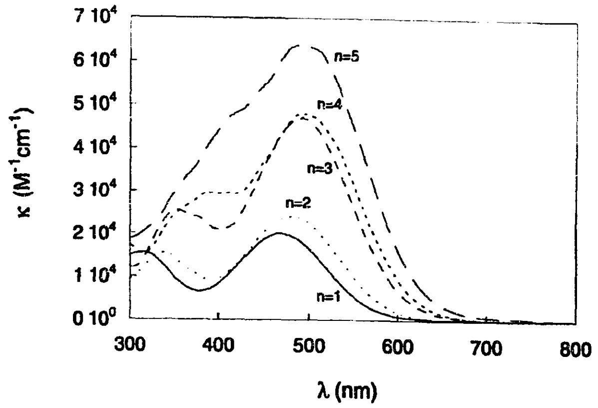


Fig. 1. UV–visible absorption spectra for push–pull diphenylpolyenes of series 3 in chloroform. κ is the molar decadic extinction coefficient.

$$F=\frac{\mu_g}{2\pi\epsilon_0 a^3}\frac{\epsilon_r-1}{2\epsilon_r+1} \qquad (3)$$

where ϵ_0 is the vacuum permittivity, ϵ_r is the solvent dielectric constant and μ_g is the solute ground state dipole. The differential stabilization of the ground state and excited state dipoles by the reaction field induces a shift in the ICT transition energy. If both the ground state dipole and the Onsager cavity radius are known, the photoinduced change in the dipole (i.e. $\Delta\mu$ value) can be extracted from absorption solvatochromism data. However, one of the main drawbacks of the solvatochromism method lies in the uncertainty in the estimation of the structural parameter a. In addition, it should be noted that the magnitude of the electric reaction field responsible for the solvatochromism of polar compounds can decrease dramatically with increasing molecular size (see Eq. (3)). As a result, the solvatochromism methodology may prove deficient for elongated molecules.

3.2. EOAM

EOAM are based on the application of an external electric field. The electric-field-induced shift of the absorption spectra of polar chromophores in solution is related to combined orientation and electrochromism processes. Thus the Onsager cavity radius has no direct influence. This explains why EOAM allow for a more reliable determination of the $\Delta\mu$ values than solvatochromism. Likewise, EOAM are clearly more appropriate for elongated chromophores since, in this case, the size effect will be mainly determined by the variations in the ground state dipole and in the photoinduced

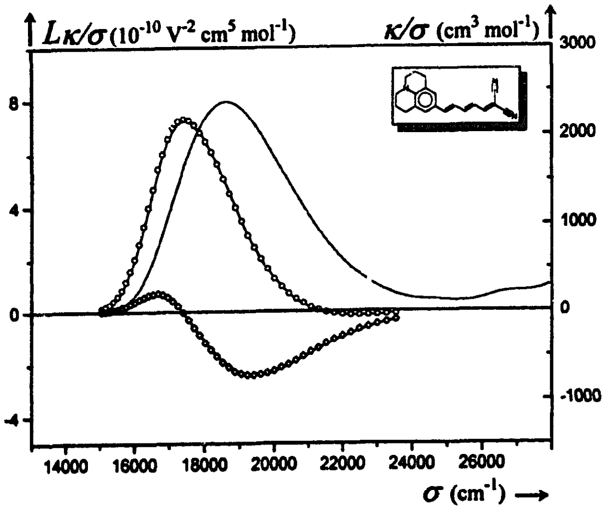


Fig. 2. Optical (κ/σ) and electro-optical ($L\kappa/\sigma$) absorption spectra of molecule **1b**[3] in dioxan at 298 K. The figure shows the experimental data points for parallel (○) and perpendicular (◇) polarization of the incident light relative to the external applied electric field and the calculated curves obtained by a general least-squares optimization.

change in the dipole without any buffering effect of increasing cavity radius.

Examples of the optical (κ/σ) and electro-optical ($L\kappa/\sigma$) spectra obtained for compound **1b**[3] are shown in Fig. 2. The excellent agreement between the experimental and approximated EOA spectra indicates that there is only one intense electronic transition contributing in the region of the lowest energy transition.

A very good agreement was also noted for push–pull phenylpolyenes of series **1a** (with $n<5$), **1b**, **1c** and **2** (with $n<5$), as well as for the shorter push–pull diphenylpolyenes of series **3** (with $n<5$). However, discrepancies between the experimental and approximated EOA spectra were observed for the longest compound of series **3**, especially in the longer wavelength region of the absorption band. Such behaviour can presumably be attributed to conformational effects in solution and/or congestion with higher energy transitions (see Fig. 1).

A regression analysis of the EOA spectrum gives information on the ground and excited state dipoles and polarizabilities of the solute, as well as on the direction of the transition dipole [1]. For push–pull molecules with significant ground state dipoles and large photoinduced changes in the dipole, polarizability contributions as well as terms originating from the field dependence of the transition dipole can be neglected. As a result, both the ground state and excited state dipole values (μ_g and μ_e) can be easily derived [4,36]. Hence EOAM conducted on molecules of series **1–3** allow for the determination of the ground state and excited state dipoles. Furthermore, they provide evidence that both are, to a good approximation, parallel to the transition dipole. The results are gathered in Table 1.

3.3. Optical non-linearities

The EFISH experiment [9–11] allows for the determination of the mean microscopic hyperpolarizability γ_0

Table 1
Maximum absorption wavelengths (λ_{max}), molar extinction coefficients (κ_{max}) and transition (μ_{ge}), ground state (μ_g) and excited state (μ_e) dipole moments of molecules of series 1–3 derived from absorption and EOAM performed in dioxan at $T=298$ K

Compound [n]	λ_{max} (nm)	κ_{max} (mol^{-1} cm^{-1})	μ_{ge} (D)	μ_g (D)	μ_e (D)	$\Delta\mu=\mu_e-\mu_g$ (D)
1a[1]	396	31700	6.5	6.6	18.1	11.5
1a[2]	426	26950	6.8	6.7	22.4	15.7
1a[3]	450	34000	8.2	7.2	27.2	20.0
1a[4]	471	48600	10.2	7.4	29.6	22.3
1a[5]	480	61000	11.8	7.8	32.9	25.1
1b[1] [a]	444	55100	7.6	9.7	18.0	8.3
1b[2] [a]	503	41450	8.3	9.8	24.3	14.5
1b[3]	534	44600	9.5	10.2	30.6	20.4
1b[4]	560	45900	10.1	10.5	33.9	23.4
1b[5]	569	56600	11.8	11.0	43.0	32.0
1c[1]	484	51000	8.2	6.8	18.6	11.7
1c[2]	514	44000	9.0	7.8	26.7	18.9
1c[3]	531	36300	8.7	7.0	29.0	22.0
1c[4]	542	42800	10.0	7.5	35.0	27.6
2[1]	490	88700	9.3	7.9	15.5	7.7
2[2]	557	80600	10.7	8.6	21.8	13.2
2[3]	583	60600	11.3	8.5	30.6	22.1
2[4]	600	62400	12.3	8.8	37.5	28.7
2[5]	610	74700	13.7	9.0	51.4	42.4
3[1]	452	26000	7.4	7.8	30.3	22.5
3[2]	466	36750	8.9	8.0	33.0	25.0
3[3]	479	45900	10.2	8.1	35.4	27.3
3[4]	484	50600	10.9	8.2	36.6	28.4
3[5]	499	59200	12.8	8.1	39.3	31.2

[a] From Ref. [5].

$$\gamma_0=\gamma(-2\omega;\ \omega,\omega,0)+\mu_g\beta(-2\omega;\ \omega,\omega)/5kT \qquad (4)$$

The first term is the scalar part of the cubic hyperpolarizability tensor, whereas the second arises from the partial orientation of the ground state dipole μ_g in the static electric field. The orientational contribution is usually assumed to be the predominant component for polar push–pull compounds. Hence the scalar product $\mu_g\beta(2\omega)$, where $\beta(2\omega)$ (a short-hand notation for $\beta(-2\omega;\ \omega,\omega)$), the vector part of the quadratic hyperpolarizability tensor, is directly inferred. The static $\mu_g\beta(2\omega)_{\mathrm{EFISH}}$ values derived from EFISH experiments carried out on molecules of series **1**–**3** are gathered in Table 2, together with the corresponding static $\mu_g\beta(0)_{\mathrm{EFISH}}$ values calculated using the two-level model to account for dispersion enhancement [12,13]. These values are compared with the $\mu_g\beta(0)_{\mathrm{EOAM}}$ values calculated from EOAM data using the two-level expression of the quadratic hyperpolarizability (see Eq. (1)). The $\beta(0)_{\mathrm{EOAM}}$ values are also given in Table 2.

4. Discussion

4.1. Effect of polyenic chain length

In each series of homologous compounds, a smooth enhancement of the transition dipole accompanies the bathochromic shift and concomitant broadening of the ICT absorption band induced by increasing the polyenic chain length (see Table 1). Such a behaviour, also observed with push–pull polythiophenes [4], is indicative of effective conjugation along the polyenic chain. In contrast, other push–pull systems, such as donor–acceptor polyphenyls or polyynes, exhibit distinct trends. For example, push–pull diphenylpolyynes exhibit ICT absorption bands whose energy and intensity appear to be relatively independent of the length of the conjugated linker [3,17]. Also, push–pull polyphenyls show first bathochromic then hypsochromic shifts with increasing number of phenyl units, the minimum ICT transition energy being observed for two or three repeating units [17,37].

As noted from Table 1, lengthening the polyenic chain linking the donor and acceptor end groups results in a marked increase in the excited state dipole. In comparison, the ground state dipole remains roughly constant. Consequently, the photoinduced change in the dipole increases significantly with increasing polyenic chain length. In each series of homologous compounds of increasing length, a linear dependence of the $\Delta\mu$ values on the number n of double bonds in the polyenic chain is obtained as illustrated in Fig. 3 for molecules of series **2**. The series of push–pull diphenylpolyenes **3**

Table 2
Quadratic molecular optical non-linearities of molecules of series 1–3 derived from EFISH experiments (carried out in chloroform at $T=298$ K) or calculated from EOAM data (obtained in dioxan at $T=298$ K)

Compound [n]	$\lambda_{\max}$ [a] (nm)	$\mu_g\beta(2\omega)_{\mathrm{EFISH}}$ (10^{-48} esu)	$\mu_g\beta(0)_{\mathrm{EFISH}}$ (10^{-48} esu)	$\mu_g\beta(0)_{\mathrm{EOAM}}$ (10^{-48} esu)	$\beta(0)_{\mathrm{EOAM}}$ (10^{-30} esu)
1a[1]	401 [b]	210 [b]	165 [b]	189	29
1a[2]	446			337	50
1a[3]	469			745	103
1a[4]	486			1443	195
1a[5]	490			2387	306
1b[1]	458	420	305	342	35
1b[2]	531	1500	955	943	96
1b[3]	572	3700	2155	2049	200
1b[4]	594	7700	4255	3034	288
1b[5]	606	10700	5735	5566	506
1b[6]	613	16000	8420	7964	724
1c[1]	494 [c]	740 [c]	505 [c]	475	70
1c[2]	542	1375	880	1195	153
1c[3]	556	2200	1330	1260	180
1c[4]	566	3800	2240	2318	309
2[1]	505 [d]	680 [d]	455 [d]	477	61
2[2]	587 [d]	2150 [d]	1210 [d]	1541	178
2[3]	641 [d]	5300 [d]	2580 [d]	3111	366
2[4]	650 [d]	9300 [d]	4400 [d]	5187	590
2[5]	659	19500	8970	9945	1105
3[1]	469	1250	890	746	96
3[2]	479	1800	1260	1294	162
3[3]	486	2440	1690	1987	246
3[4]	494	3580	2440	2440	299
3[5]	497	4300	2920	3863	477

[a] In chloroform.
[b] From Ref. [14] in acetone.
[c] In acetone.
[d] From Ref. [24].

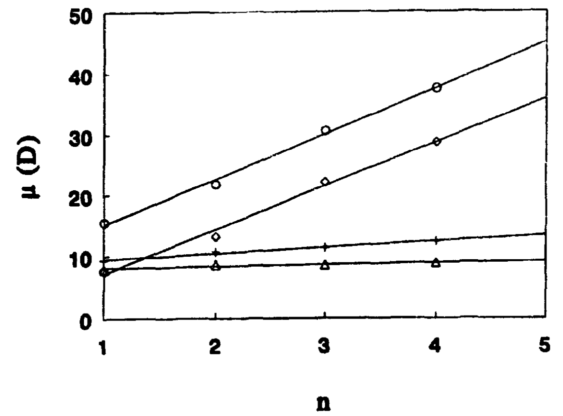


Fig. 3. Effect of increasing number of double bonds *n* in the polyenic chain on the transition dipole (μ_{eg}, +), ground state dipole (μ_g, △), excited state dipole (μ_e, ○) and photoinduced change in the dipole ($\Delta\mu$, ◇) for compounds of series **2**.

shows the smoothest variation (with a vinylic increment of about 2 D). In contrast, the steepest rise is observed with push–pull phenylpolyenes of series **2** (with a vinylic increment of about 8.5 D) which have the strongest electron-withdrawing group. As a result, molecule **2**[5] exhibits a very high $\Delta\mu$ value (42 D) that corresponds to more than half of an electronic charge shifted on excitation from the donor substituent to the opposite acceptor over 16 Å.

As seen in Table 2, lengthening the polyenic chain results in a pronounced increase in quadratic optical non-linearities. In addition, both the length dependence and the magnitude of the optical non-linearities depend strongly on the nature of the end group. This is clearly shown in Fig. 4 where the variations of the $\mu_g\beta(0)_{\mathrm{EFISH}}$ values as a function of the number *n* of conjugated double bonds in the polyenic chain are shown. The series of push–pull diphenylpolyenes **3** shows the slowest variation, whereas the series of push–pull phenylpolyenes with the strong acceptor end group **2** shows the steepest rise in quadratic non-linearities. This phenomenon leads to a giant $\mu_g\beta(0)$ value for molecule **2**[5], amounting to 20 times that of 4-dimethylamino-4′-nitrostilbene (DANS), the benchmark for quadratic non-linear optics. It should be noted that this is particularly interesting since the $\mu\beta(0)$ value is the relevant figure of merit for using such molecules as active elements in poled-polymer-based devices for electro-optical modulation.

4.2. Validity of the two-level approximation

Comparison of the $\mu_g\beta(0)_{\mathrm{EFISH}}$ and $\mu_g\beta(0)_{\mathrm{EOAM}}$ values listed in Table 2 indicates that the $\mu_g\beta$ values derived from EFISH experiments or calculated from EOAM data (using the two-level approximation) display acceptable correlation, except for a few molecules (i.e. **1b**[4], **1c**[2] and **3**[5]). This demonstrates that the two-level model is fairly relevant for push–pull polyenes. The slight discrepancies observed can be accounted for by several origins. For instance, it should be stressed that EFISH experiments and EOAM were conducted in solvents of different polarity. Likewise, the simplifications commonly used in the treatment of EFISH data to derive static $\mu_g\beta(0)$ values (e.g. the neglect of the cubic contribution, the local field corrections and the approximate dispersion correction) are potential sources of inconsistency. Another possibility is the involvement of higher excited states contributing significantly to the optical non-linearities. This may be the case for the series of diphenylpolyene derivatives **3**, as suggested by the emergence of a higher energy transition which moves closer to the high-energy edge of the ICT absorption band (see Fig. 1).

4.3. Effects of end groups

As mentioned previously, the nature of the end groups has been found to influence strongly the β and $\Delta\mu$ length dependences. The series of push–pull diphenylpolyenes **3** clearly shows the smoothest length behaviour (cf. Fig. 4 and Fig. 5). This effect may possibly be related to the presence of phenyl rings in between the donor and acceptor substituents and the polyenic chain. The aromatic stabilization of the benzene ring is responsible for electron localization, therefore dampening the donor–acceptor interaction.

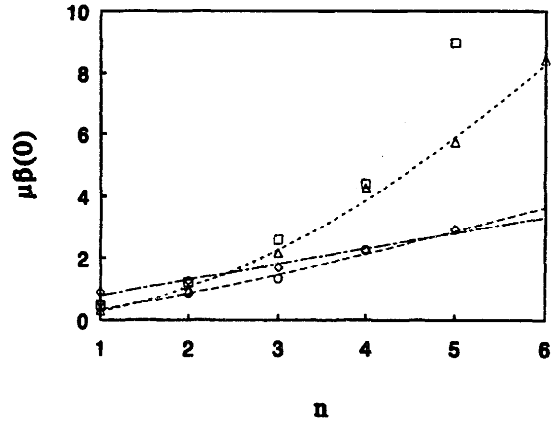


Fig. 4. $\mu\beta(0)$ values determined by EFISH experiments vs. the number *n* of double bonds in the polyenic chain for series **1b** (△, – – –), **1c** (○, ————), **2** (□, - - -) and **3** (◇, — — —); all $\mu\beta(0)$ values are expressed in 10^{-45} esu.

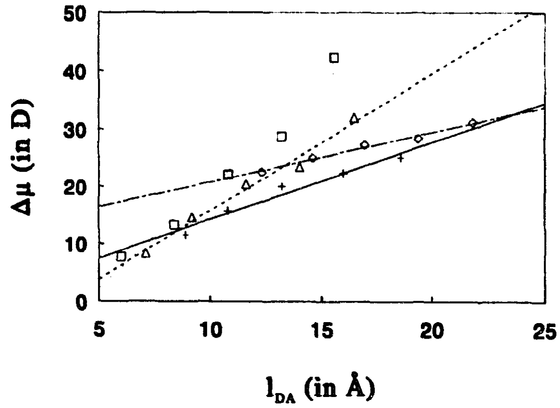


Fig. 5. Photoinduced change in the dipole ($\Delta\mu$ values) as a function of the length (l_{DA}) between donor and acceptor for series **1a** (+, ————), **1b** (△, – – –), **2** (□, - - -) and **3** (◇, — — —).

The series of push–pull phenylpolyenes displays a steeper length behaviour, the rise in both the $\Delta\mu$ and $\mu\beta(0)$ values being steeper for stronger acceptor end groups. For instance, the vinylic increment of the photoinduced change in the dipole amounts to 3.5 D per additional double bond for series **1a**, 5.5 D for series **1b** and 8.5 D for series **2**, in agreement with increasing acceptor strength. In comparison, a vinylic increment of only 2 D is observed for the series of push–pull diphenylpolyenes **3**. Likewise, comparison of the series of push–pull phenylpolyenes **1** and **2** shows that a stronger donor–acceptor interaction leads to a bathochromic shift of the ICT absorption band as well as to enhanced quadratic optical non-linearities (see Table 2).

In order to study the influence of the donor/acceptor strength on the magnitude of the photoinduced change in the dipole, $\Delta\mu$ values were plotted for series **1**–**3** as a function of the separation length between the closest heteroatoms from donor and acceptor moieties (calculated for an extended conformation of the polyenic chain). As indicated in Fig. 5 for the series of push–pull phenylpolyenes **1** and **2**, increasing donor/acceptor strength leads to larger $\Delta\mu$ values. On the other hand, a direct comparison with the series of push–pull diphenylpolyenes **3** is not straightforward. Altogether, given the markedly different length dependences, the largest $\Delta\mu$ values are expected for elongated push–pull phenylpolyenes compared with push–pull diphenylpolyenes. This is illustrated by examination of molecule **2**[5], which shows a larger photoinduced change in the dipole (i.e. 42.4 D) than molecule **3**[5] (i.e. 31.2 D), although corresponding to a 6 Å smaller distance between donor and acceptor heteroatoms.

5. Conclusions

This work demonstrates that push–pull polyenes allow for long-distance and low-energy photoinduced ICT. In each series of homologous compounds, lengthening the polyenic chain linking the donor and acceptor end groups induces a bathochromic shift of the ICT absorption band as well as a smooth increase in the transition dipole. Moreover, a pronounced increase in the excited state dipole is observed, whereas the ground state dipole remains roughly unchanged. Accordingly, the longest molecules exhibit very large photoinduced changes in the dipole moment (with $\Delta\mu$ values up to 42 D) as well as enhanced quadratic optical non-linear hyperpolarizabilities (with $\mu_g\beta(0)$ values up to 20 times that of DANS).

The nature of the end groups has been found to influence strongly both ICT and optical non-linearities. Steeper length dependences were obtained for push–pull phenylpolyenes with strong acceptors, which also led to the largest optical non-linearities. Finally, lengthening the polyenic chain, as well as increasing the strength of the donor and acceptor end groups, is a highly effective strategy for enhancing photoinduced charge transfer.

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