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Chain flexibility and nonlinear optical properties in polyenes within a two-state (VB-CT) model

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Abstract

We present a simple two-state model that justifies the dependence of first-order hyperpolarizabilities (β) of push–pull polyenes on conformational disorder. Particular relevance is given to the calculation of the vibrational properties (i.e. force constants, infrared and Raman intensities) which are used for the evaluation of the vibrational contribution to static molecular hyperpolarizabilities. The theoretical predictions are compared with experimental measurements of the quantities of interest on suitable molecules purposely synthesized.

1. Introduction

Push–pull chromophores have been extensively studied in the recent past because of their potential in second-order n.l.o. applications [1–3] (and references therein). The common feature of these systems is the presence of a donor group (D) coupled, through a π-conjugated bridge, to an acceptor group (A).

The push–pull polyene molecules studied in this work are presented in Fig. 1. Molecules 1b and 1c are obtained from molecule 1a by addition of respectively two and one saturated rings (hereafter referred to as σ-bridges) which, in a first approximation, should not induce any electronic perturbation onto the main unsaturated chain; molecules 2b and 2c are obtained from molecule 2a by addition of respectively three and two similar bridges. The purpose of this work is the study of the effect of such substitution on the structure and properties of the molecules.

The question of planarity in polyconjugated systems has been matter of active discussion for many years. A planar backbone should favor delocalization of the π-electrons and hence increase the conjugation length. Especially in polyaromatic and heteroaromatic systems, where rotation around single CC bond in the chain is quite easy, the conformational problem has been widely studied [4–6]. With much stiffer polyene chains the problem of chain flexibility should be less severe. However it is not possible to rule out (i) the existence of small deviations from perfect planarity, which have been vaguely defined as twistons or conformons [7] and/or (ii) the existence of large amplitude torsional vibrations. The introduction of ''σ-bridges'' in the polyene systems studied in this work should increase the conformational rigidity of the polyene chain and should remove the conformational

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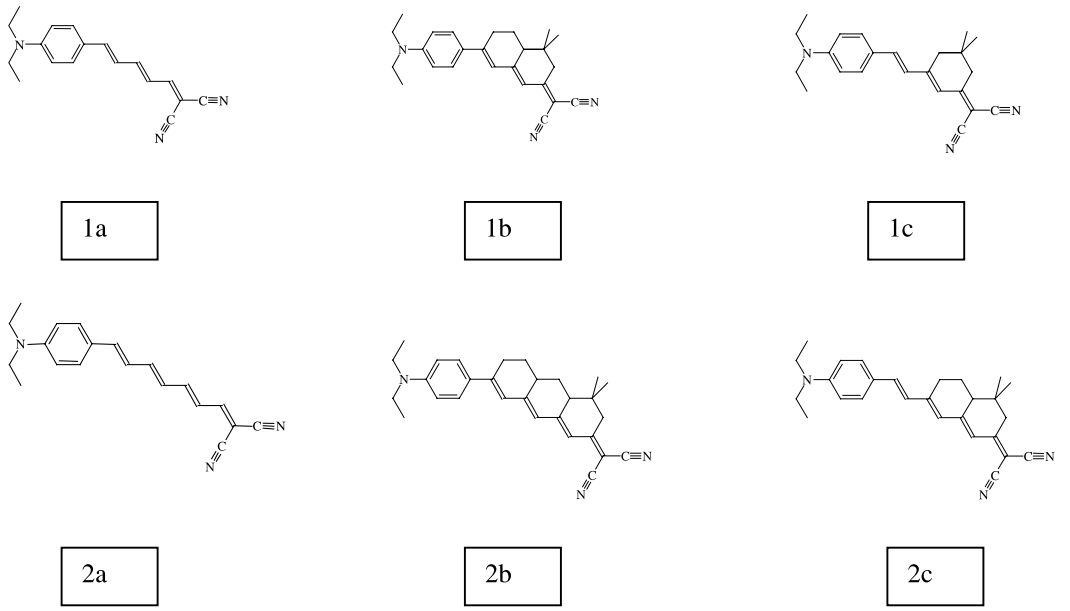


Fig. 1. Molecules considered in this work.

effects quoted above. Similar groups occur also in the extremely long polyene chains recently synthesized by Scrock and coworkers [8] and their influence on the n.l.o. properties of these materials is still matter of study. In the case of push–pull systems in addition to the question of effective conjugation length, deviations from planarity can affect the extent of charge transfer from the donor to the acceptor group resulting in less effective polar end groups.

Purpose of this work is a careful study of the effect of the increasing rigidity in push–pull polyenes on the molecular properties with special attention to molecular first hyperpolarizabilities (β).

The analysis will be carried out with the help of the vibrational spectra which will be used for the measure of the vibrational contribution to hyperpolarizabilities. Moreover the experimental results will be rationalized in the frame of a two-state model described in the following section.

2. Two-state model

The valence-bond charge-transfer (VB-CT) model has been recently used in the literature, by several authors, in order to express analytically the dependence from a few structural parameters of various molecular properties of push–pull systems. Among these, molecular hyperpolarizabilities, which are the center of interest for molecular photonics, are of particular interest for this work. These parameters describe the energy of the two states (VB and CT) and their coupling in the Hamiltonian [9–14]. Within this model it has been possible to explicitly introduce the dependence of molecular properties on a particularly meaningful structural parameter, namely the bond length alternation (BLA). Assuming that there exists only one vibrational coordinate, q, which describes oscillations of BLA, it is easy to relate the molecular properties to the structural parameter q_{eq} defined as the equilibrium value taken by q in the ground state. Such a coordinate is given by the in-phase stretching of the double CC bonds and shrinking of the single CC bonds:

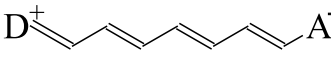
$$q = \frac{1}{\sqrt{N_{C=C}}}\left(\sum_{1}^{N(C=C)} R_{C=C} - \sum_{1}^{N(C-C)} r_{C-C}\right). \qquad (1)$$

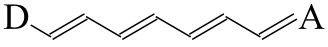
This vibrational coordinate has been widely used in the past by the authors in order to describe the

spectroscopic behavior of polyconjugated systems and is usually referred to as "я" [15,16].

In the VB-CT model it is possible to describe the electronic wave function η as a linear combination of the two canonical wave functions η_{VB} and η_{CT} corresponding to the VB and CT states:

$$\eta = c_1\eta_{VB} + c_2\eta_{CT}. \tag{2}$$





In this work we assume that in the VB state $q_{eq} = q^0_{VB} = -0.12$ Å and in the CT state $q_{eq} = q^0_{CT} = 0.12$ Å. (Based on the experimental observations of the average bond lengths of *trans*-1,3,5,7-octatetraene [17].)

Given a certain molecule, i.e. chosen A, D, and the conjugated bridge, its structure in the electronic ground state will turn out to be intermediate between those in the VB and CT states and can be determined with the following reasoning.

In the harmonic approximation it is possible to write:

$$\begin{aligned} E_{VB} &= \tfrac{1}{2}k(q - q^0_{VB})^2, \\ E_{CT} &= V_0 + \tfrac{1}{2}k(q - q^0_{CT})^2, \end{aligned} \tag{3}$$

where k represents the force constant relative to the vibrational coordinate q in the VB and CT states and V_0 is the energy difference between the minima of E_{VB} and E_{CT}.

Solving the electronic Hamiltonian H_{el} and using the orthogonality of η_{VB} e η_{CT} together with Eq. (3) yields for the electronic ground state $\varepsilon_g(q)$:

$$\begin{aligned} \varepsilon_g(q) = \frac{1}{2}\left[V_0 + \frac{1}{2}k(q - q^0_{CT})^2 + \frac{1}{2}k(q - q^0_{VB})^2\right] \\ - \frac{1}{2}\left[(kq(q^0_{VB} - q^0_{CT}) + V_0)^2 + 4t^2\right]^{1/2}, \end{aligned} \tag{4}$$

where the transfer integral t is defined as:

$$t = \int \eta^*_{CT} H_{el} \eta_{VB}\, d\tau = \int \eta^*_{VB} H_{el} \eta_{CT}\, d\tau;$$

$$H_{el} = \begin{bmatrix} E_{VB} & t \\ t & E_{CT} \end{bmatrix}. \tag{5}$$

q_{eq} can be found by minimizing the ground state energy with respect to q. In this way it is possible to find a relationship between V_0 and q_{eq}. In Fig. 2 we report the plot of V_0 versus q_{eq} for $k = 33.55$ eV/Å^2 and $t = 1.1$ eV.

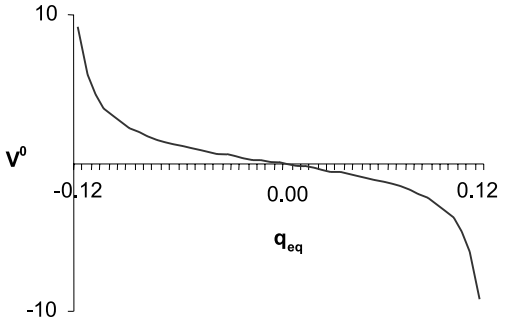


Fig. 2. Plot of V^0 as function of the equilibrium value of the q coordinate in the VB-CT model (see text).

Large, positive V_0 values correspond to q_{eq} close to the VB (polyenic) structure, while large, negative V_0 values correspond to q_{eq} close to the CT (zwitterionic) structure.

The presence of an electric field F_z in the chain axis direction, modifies the difference between the energy minima (V_F) according to:

$$V_F = V_0 - \mu^{CT}_z F_z, \tag{6}$$

μ^{CT} is the dipole moment in the CT state, while one can assume $\mu^{VB} = 0$. It thus follows that the electronic energy of the ground state under the action of an electric field is simply given by Eq. (4) with V_F instead of V_0. The successive derivatives of the electronic energy with respect to the applied field yield the expressions of the dipole moment μ^{el-g}, of the electronic polarizability α^{el-g} and of the first-order hyperpolarizability β^{el-g}:

$$\begin{aligned} \mu^{el-g}_z(q) &= -\frac{d\varepsilon_g(q)}{dF_z}\Big|_0 \\ &= \mu^{CT}_z\left\{\frac{1}{2} - \frac{k\Lambda q + V_0}{2[(k\Lambda q + V_0)^2 + 4t^2]^{1/2}}\right\}, \end{aligned} \tag{7}$$

$$\begin{aligned} \alpha^{el-g}_{zz}(q) &= -\frac{d^2\varepsilon_g(q)}{dF_z^2}\Big|_0 \\ &= 2\frac{(\mu^{CT})^2 t^2}{[(k\Lambda q + V_0)^2 + 4t^2]^{3/2}}, \end{aligned} \tag{8}$$

$$\beta_{zzz}^{\mathrm{el-g}}(q) = -\frac{\mathrm{d}^3\varepsilon_{\mathrm{g}}(q)}{\mathrm{d}F_z^3}\Big|_0 = 6\frac{(\mu^{\mathrm{CT}})^3 t^2 (k\Lambda q + V_0)}{[(k\Lambda q + V_0)^2 + 4t^2]^{5/2}}, \quad (9)$$

where $\Lambda = q_{\mathrm{VB}}^0 - q_{\mathrm{CT}}^0$. From Eqs. (7)–(9) it follows that $\mu^{\mathrm{el-g}}$, $\alpha^{\mathrm{el-g}}$, and $\beta^{\mathrm{el-g}}$ depend parametrically on the nuclear coordinate q. Recalling that infrared and Raman intensities are respectively proportional to the square of the dipole moment and polarizability derivatives with respect to the normal coordinate:

$$I_{\mathrm{IR}} \div \left(\frac{\partial\mu^{\mathrm{el-g}}}{\partial q}\Big|_{\mathrm{eq}}\right)^2 \text{ and } I_{\mathrm{Ram}} \div \left(\frac{\partial\alpha^{\mathrm{el-g}}}{\partial q}\Big|_{\mathrm{eq}}\right)^2$$

one obtains:

$$\frac{\partial\mu_z^{\mathrm{el-g}}}{\partial q}\Big|_{\mathrm{eq}} = -\frac{2k\Lambda t^2\mu^{\mathrm{CT}}}{[(k\Lambda q_{\mathrm{eq}} + V_0)^2 + 4t^2]^{3/2}}, \quad (10)$$

$$\frac{\partial\alpha_{zz}^{\mathrm{el-g}}}{\partial q}\Big|_{\mathrm{eq}} = -\frac{6k\Lambda(k\Lambda q_{\mathrm{eq}} + V_0)t^2(\mu^{\mathrm{CT}})^2}{[(k\Lambda q_{\mathrm{eq}} + V_0)^2 + 4t^2]^{5/2}}. \quad (11)$$

The dependence of the infrared and Raman intensities on q_{eq} are shown in Fig. 3.

We have recently shown that with the vibrational method [18,19] it is possible to measure the vibrational contribution to molecular hyperpolarizabilities from the knowledge of the absolute infrared, Raman and hyper-Raman intensities. For example, in the case of the first-order polarizability, the component along the chain axis is given by:

$$\beta_{zzz}^{\mathrm{vib-0}} = \frac{3}{k_{\mathrm{g}}}\frac{\partial\mu_z^{\mathrm{el-g}}}{\partial q}\Big|_{\mathrm{eq}}\frac{\partial\alpha_{zz}^{\mathrm{el-g}}}{\partial q}\Big|_{\mathrm{eq}}, \quad (12)$$

where k_{g} is the force constant of the vibrational normal mode q. Since by definition:

$$k_{\mathrm{g}} = \frac{\partial^2\varepsilon_{\mathrm{g}}(q)}{\partial q^2}\Big|_{\mathrm{eq}}, \quad (13)$$

k_{g} is no longer a constant but depends on the value taken by q_{eq}. The variation of the force constant with respect to the values taken in the VB and CT forms becomes very large the less alternated is the chain. The comparison of $\beta_{zzz}^{\mathrm{vib-0}}$ and $\beta_{zzz}^{\mathrm{el-g}}$ obtained from Eqs. (9) and (12) is shown in Fig. 4. It must be noted that in the expression of all the electronic quantities, namely $\mu_z^{\mathrm{el-g}}$, $\alpha_{zz}^{\mathrm{el-g}}$ and $\beta_{zzz}^{\mathrm{el-g}}$, as well as infrared and Raman intensities, k assumes the constant value of the VB and CT forms. On the contrary in the expression for $\beta_{zzz}^{\mathrm{vib-0}}$ there is an explicit dependence on the vibrational frequency ν ($4\pi^2c^2\nu = k_{\mathrm{g}}$ in the hypothesis of only one normal mode). It is well known that [15,20] the vibrational frequency of the skeletal modes of π-systems is very sensitive to the electronic distribution and softens as one considers more delocalized systems. For this reason, the use of a force constant k independent of q, is no longer justified. It must be noted that if k_{g} is assumed constant, the qualitative behavior of $\beta_{zzz}^{\mathrm{vib-0}}$ is much more similar to that of $\beta_{zzz}^{\mathrm{el-g}}$ (see Fig. 4). This observation might explain why in the limit of cyanine-like systems the agreement between vibrational and electronic hyperpolarizabilities is not as good as in the polyenic limit [21]. For example in Table 1 the ab initio calculated (3-21G) β_μ^{v} and β_μ^{e} for different push–pull molecules are reported. The extremely good agreement found for the more polyene-like systems becomes less satisfactory in the case of the strongest push–pull compound of the series (IV).

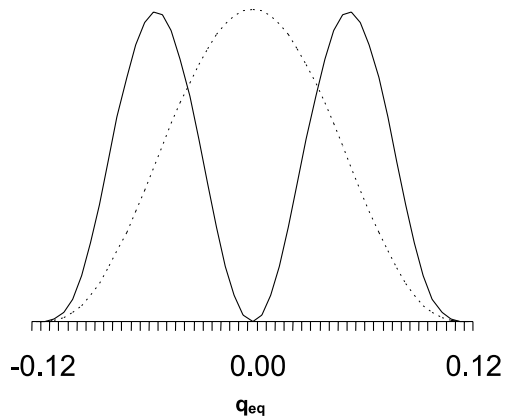


Fig. 3. Evolution of infrared (···) and Raman (—) intensities with q_{eq} in the VB-CT model (see text).

3. The two-state model: solvatochromism and conformational dependence

The parameters of the two-state model as applied to push–pull systems, depend on the choice

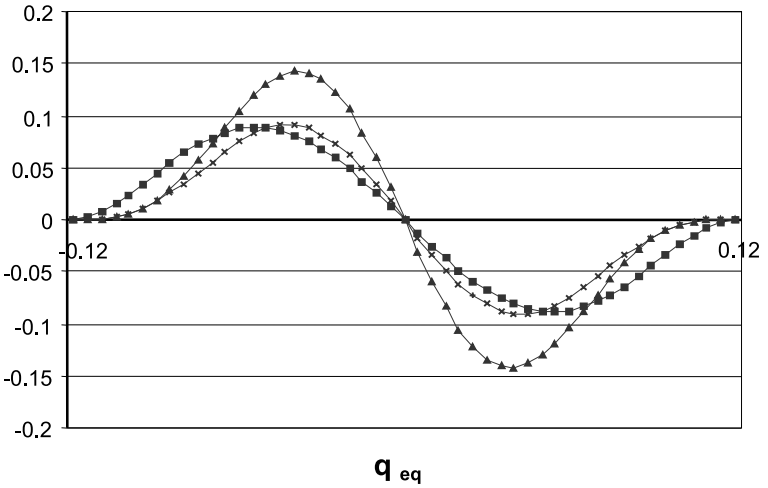
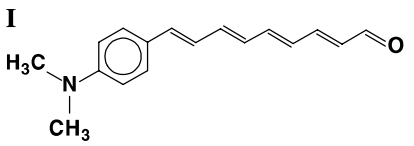
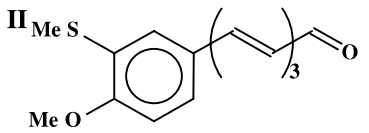
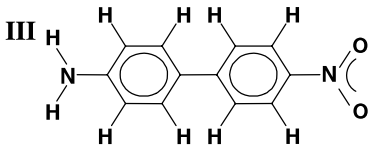
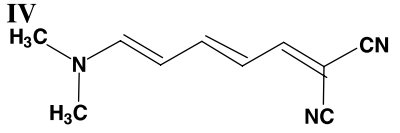


Fig. 4. Comparison of β^{e} (■), β^{v}_{kg} (▲) and β^{v}_{k} (✖) (see text).

Table 1
Comparison between ab initio calculated (RHF 3-21G) β^{v}_{μ} and β^{e}_{μ} of various push–pull polyene systems with increasingly strong polar end groups (values are in esu)

	β^{v}_{μ}	β^{e}_{μ}
I 	7.33E−29	7.43E−29
II 	3.47E−29	3.20E−29
III 	2.82E−29	3.10E−29
IV 	8.35E−29	3.07E−29

of the donor and acceptor group as well as on the kind and length of the conjugated bridge. Once we have chosen a molecule of given A, D and π-system we can again modify the parameters by acting

on the surrounding medium (solvent, matrix effect) or inducing structural changes in the isolated molecule (conformational distortions).

The solvent effect has been widely studied [22–26]. It is well known that it is possible to stabilize the CT form by using solvents of increasing polarity. In so doing it is possible to tune the molecular properties by changing the value of q_{eq} in a continuous way from the polyenic to the zwitterionic structure.

In the presence of a solvent we can generalize the two-state model by substituting V_0 of the isolated molecule with V_S, a new parameter which takes into account the interaction with the solvent. Necessarily, if we wish to move towards the zwitterionic limit (increasing q_{eq}) V_0 must decrease (see Fig. 1) and hence $V_S < V_0$. As a consequence all the molecular properties discussed in the previous section must change.

The second way to modify the molecular structure, and this is the major concern of this work, is through conformational distortions.

Experimentally a torsion around a given bond can be induced by steric hindrance with neighboring atoms. Within a simple Hückel theory, in the simplest π-molecule, i.e. ethylene, the energy ε_{+1} of the highest occupied level ψ_{+1} is given by [27,28]:

$$\varepsilon_{+1} = \alpha + \beta, \tag{14}$$

where α is the Coulomb integral of a carbon atom and $\beta(<0)$ is the resonance integral of a CC bond. A torsion around the π-bond lessens the overlap between π-orbitals and β decreases in modulus. The dependence of β on the torsional angle is often assumed to be given by [28]:

$$\beta(\vartheta) = \beta\cos(\vartheta). \tag{15}$$

In the two-state model described above when $E_{VB} < E_{CT}$ $(V > 0)$ a torsion θ around a single CC bond in the VB state does not change the π-energy, i.e. $E_{VB}(\theta = 0) = E_{VB}(\theta)$.

In the CT state a torsion around the same bond (a double bond) yields an energy change given by:

$$E_{CT}(\theta) - E_{CT}(\theta = 0) = 2(\alpha + \beta\cos\theta) - 2(\alpha + \beta) = 2\beta(\cos\theta - 1), \tag{16}$$

Setting

$$V = E_{CT}(\theta = 0) - E_{VB}(\theta = 0),$$

and

$$V_\theta = E_{CT}(\theta) - E_{VB}(\theta),$$

Eq. (16) becomes

$$V_\theta = V + 2\beta(\cos\theta - 1). \tag{17}$$

Eq. (17) $(\beta < 0, 0 < \theta < 90°)$ implies that the energy difference between the two limiting states increases, and being $V_\theta > V$ it follows that $q^\theta_{eq} < q_{eq}$ (see Fig. 2). In other words a torsion around a single bond induces a change in the electronic structure towards the polyenic limit.

With the same reasoning it can be shown that a torsion around a double CC bond produces the opposite effect i.e.

$$E_{CT}(\theta = 0) = E_{CT}(\theta),$$

and

$$E_{VB}(\theta) - E_{VB}(\theta = 0) = 2\beta(\cos\theta - 1).$$

It follows then

$$V_\theta = V_0 - 2\beta(\cos\theta - 1).$$

In this case a torsion around a double bond reduces the difference between the energy in the two limiting states and $V_\theta < V$. This means that we have a stabilization of the zwitterionic structure $(q^\theta_{eq} > q_{eq})$.

In the next section we apply these concepts to the molecules under study and we rationalize the results obtained in terms of conformational disorder induced by proper functionalization of push–pull polyene molecules.

4. Experimental

The synthesis of the compounds 1a–2c is reported elsewhere [29,30].

The FTIR spectra have been recorded with a Nicolet Magna-560 interferometer and the FT-Raman spectra ($\lambda_{exc} = 1064$ nm) have been recorded with a Nicolet 910 spectrometer.

The absorption spectra in the UV/Vis have been recorded with a Jasco-V570 spectrophotometer.

The determination of the absolute intensities has been carried out in chloroform solution, according to the procedure illustrated in Ref. [19], integrating over all the spectral pattern in a given frequency range without attempting band separation and choosing a suitable baseline.

5. Results and discussion

The experimental results will be interpreted within the frame of the two-state model described in Section 2. It must be stressed that in the following the parameters entering the model have not been optimized for the molecules treated.

A preliminary observation is that no *trans–cis* isomerization is likely to occur since the σ-bridged compounds are locked in the *trans* configuration.

The first experimental data that can be analyzed are those that can be obtained from the electronic spectra. From these data we can measure the energy gap as a function of solvent polarity. The experimental data are reported in Fig. 5a. The VB-CT model predicts the dependence of the energy gap E_{gap} on q_{eq} given in Fig 5b. Experimentally (Fig. 5a) we find that the energy gap decreases when increasing the dielectric constant of the

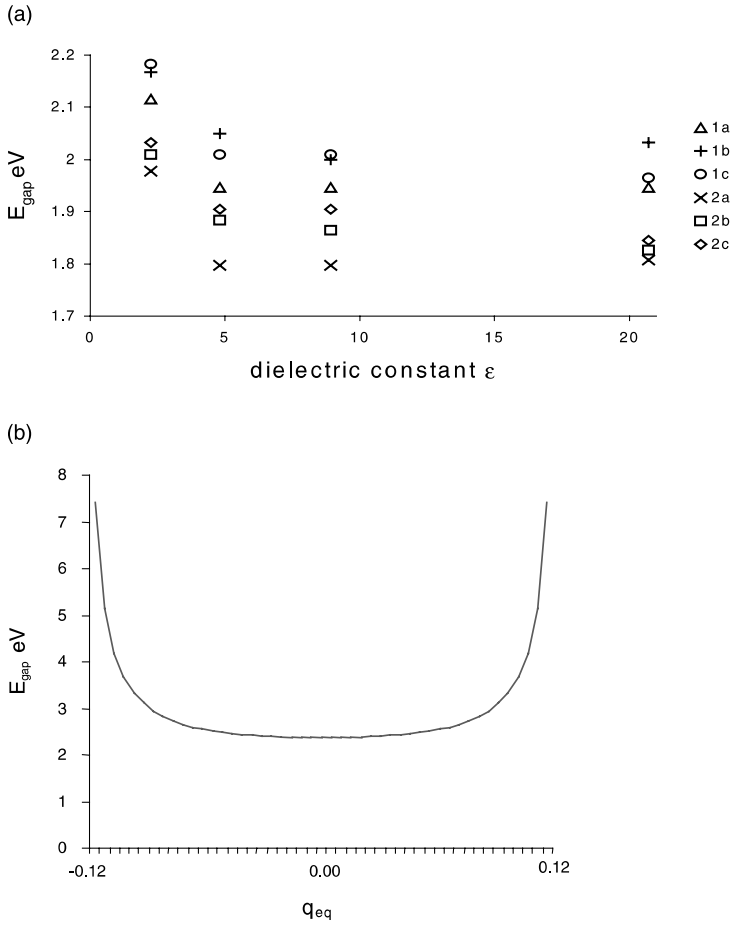


Fig. 5. (a) Experimental energy gap in various solvents for molecules 1a–1c and 2a–2c. (b) Evolution of the energy gap with q_{eq} in the VB-CT model (see text).

solvent. Indeed, polar solvents stabilize charge transfer thus allowing the molecule to become more zwitterionic (less alternated). This is true for all the molecules considered and can be interpreted as an indication that the structure of the isolated molecules is polyenic ($-0.12 < q_{eq} < 0$).

We can then observe that the molecules of series 2, longer than the molecules of series 1, systematically have a lower energy gap. This is obvious in a contest of a larger conjugation length and is consistent with a more equalized structure, i.e.:

$$q_{eq}^{\text{series 1}} < q_{eq}^{\text{series 2}}.$$

Moreover we observe that molecules with σ-bridges (1b and 1c) have larger E_g with respect to the molecule with no methylene unit (1a); the same consideration holds in the case of the second series of molecules. This means that:

$$q_{eq}^{b,c} < q_{eq}^{a}.$$

The conclusion that must be inferred is that the addition of σ-bridges induces an electronic charge perturbation in the direction of a more alternated molecular structure. This effect can be reasonably obtained by a conformational distortion around the CC bond adjacent to the σ-bridge forced by the steric hindrance between the hydrogen atoms which are facing each other at a distance less than the van der Waals radius (1.2 Å). This is a common fact in many polyconjugated aromatic and heteroaromatic polymers and even in very simple oligomers (see for example Ref. [31]).

Also the experimental vibrational intensities can be used to infer the structural information required. The effect of considering samples dissolved in more polar solvents on the vibrational spectra, is that of a lowering of the vibrational frequency of the skeletal modes (these are the normal modes which play the role of the q coordinate of the previous discussion) since a more equalized chain structure corresponds to a lower value of k_g. For example in Fig. 6 we compare the Raman spectra of molecule 2a dissolved in carbon tetrachloride and chloroform. An even larger shift is observed in the spectrum of the solid; in this case the molecules can be thought of, as dissolved in like molecules so that the interaction with the surrounding medium is the highest conceivable.

We have measured the absolute infrared and Raman intensities of all the molecules considered in various solvents. If we consider the sum of the infrared intensities (I_{IR}^{q}) and that of the Raman cross-sections ($|R_q|^2$) of all the normal modes (Q_q^*) with a high content of the q coordinate, we observe a decrease of both quantities in going, for example, from molecule 2a to molecule 2c (see Fig. 7). This means that the addition of the σ-bridges (see

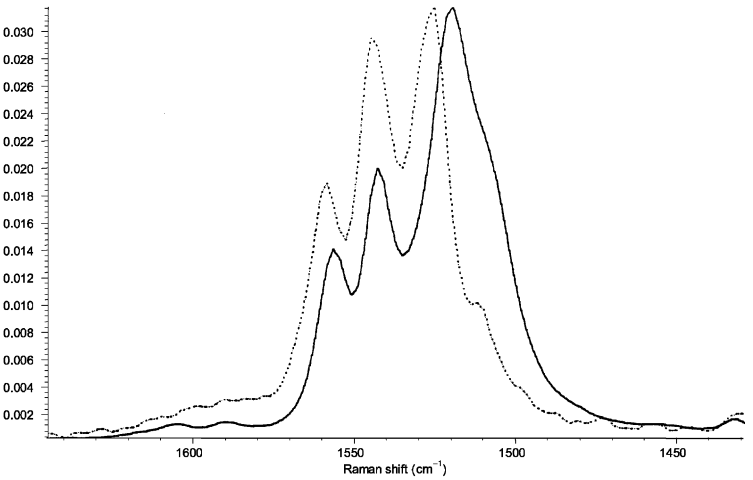


Fig. 6. Comparison of the Raman spectra of molecule 2a dissolved in chloroform (—) and carbon tetrachloride (- - -).

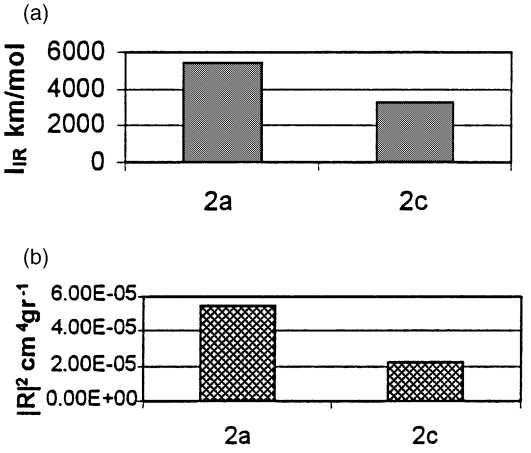


Fig. 7. Experimental infrared (a) and Raman (b) intensities of molecules 2a and 2c in the spectral region of interest (see text).

Fig. 3) makes the structure more polyene like (alternated, $-0.12 < q_{eq} < -0.055$ Å) ($q_{eq}^{2b,2c} < q_{eq}^{2a}$) and this again suggests the existence of a torsion induced by the chemical modification of molecule 2a. Such a behavior of vibrational intensities must affect β_{zzz}^{vib-0}. Since the value of β_{zzz}^{vib-0} depends on the activity of the same normal mode both in the infrared and Raman spectra a lowering of β_{zzz}^{vib-0} is expected. The effect of the addition of methylene units must then be that of a decrease in β_{zzz}^{vib-0}.

This is indeed what is found for the two series of molecules as shown in Fig. 8. Both molecules 1b and 1c, and molecules 2b and 2c, have lower β_{zzz}^{vib-0} than respectively molecules 1a and 2a.

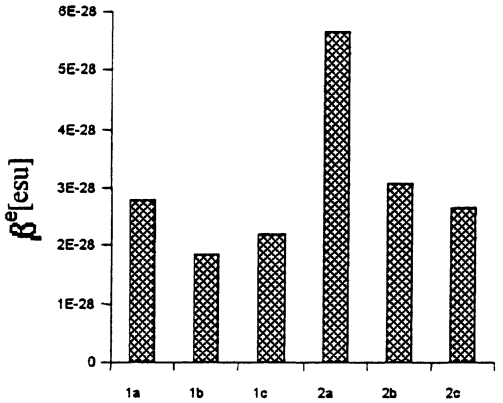


Fig. 8. Experimental β^v of molecules 1a–1c and 2a–2c.

In a similar way we would expect a decrease in β_{zzz}^{e-g}. Ab initio quantum chemical calculations (6-31G*) give for the isolated molecule (1a) $\beta_{\mu}^{vib-0} = 2.8 \times 10^{-28}$ esu and $\beta_{\mu}^{e-g} = 9.7 \times 10^{-29}$ esu in good agreement with each other and with the experimental value (molecule 1a in chloroform) $\beta_{zzz}^{vib-0} = 2.3 \times 10^{-28}$ esu.

6. Conclusions

We have tried to rationalize by a two-state model the behavior of few electronic molecular properties as function of structural changes. In the case discussed the addition of σ-bridges to the polyene chain seems to induce a skeletal distortion opposing delocalization. This can be explained by conformational disorder around the single CC bond closest to the σ-bridge induced by steric hindrance. The clue that can be inferred is that given a certain molecular structure it is possible to modulate its electronic properties not only by modifying the surrounding environment but also by constraining the molecular structure. In this particular case we are forced to exclude the existence of long, gentle distortions perturbing a large portion of the molecule (twistons) such as those introduced to explain chain diffusion in polymethylene systems (e.g. polyethylene) [32] but we are in presence of a large angle torsional deformation around one of the backbone CC bonds. Conformational disorder may not always be detrimental. For example if one could devise molecular push–pull systems in which a distortion (around a double CC bond) stabilizes charge separation [33] this could improve the molecular properties (e.g. lower energy gap, larger vibrational intensities, larger molecular vibrational and electronic polarizabilities).

Conformational regularity is an additional concept which must be kept in mind when designing molecular chromophores for n.l.o. applications. Useful indications on conformational order can be obtained directly from vibrational spectra. The related change of intensities yields a modulation of β^v. In all those cases when β^e and β^v are strictly related, this can be taken as an evidence of the extent of the change in β^e.

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