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Electronic first hyperpolarizability of polymethineimine chains with donor and acceptor groups

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Abstract

The static first hyperpolarizability of push–pull compounds based on the polymethineimine asymmetric unit cell has been investigated within a CHF/6-31G scheme. For push–pull pairs of small strength, the use of an asymmetric (polymethineimine) segment instead of a symmetric (polyacetylene) segment results in an increase of the first hyperpolarizability, whereas the opposite is true when using strong donor and acceptor groups. These effects have been explained as the consequence of the interplay between asymmetry and delocalization effects. We use the Hammet σ parameters in order to quantify the susceptibility with respect to the first hyperpolarizability of substituted polyacetylene and polymethineimine chains. Moreover the evolution with chain length of the first hyperpolarizability per unit cell of α,ω-nitro-amino polymethineimine was studied and compared to the non-substituted polymethineimine chains.

Keywords: Hyperpolarizability; Hartree–Fock method; Push–pull compounds; Polymethineimine chains

1. Introduction

The evaluation of nonlinear optical (NLO) properties and its interpretation by means of structure–property relationships are efficiently carried out by a quantum chemistry procedure [1–3]. Many theoretical works have focused on the evaluation of the first hyperpolarizability, β, of organic molecules which are candidate compounds for devices such as frequency doublers. Molecules which present large β values are generally constituted by a conjugated segment end-capped by acceptor and donor groups. Numerous donors, acceptors and linkers have already been tested both experimentally and theoretically [3]. Sum-over-states (SOS) [4] expressions of β derived from perturbation theory [5] have often been used to trace the most contributing optical excitation processes [6–12]. The uncoupled Hartree–Fock (UCHF) procedure is the simplest SOS scheme which does not include the field-induced electron reorganizational effects on the electron–electron interactions [13–15]. Improvements of this model are brought when using truncated CI schemes to determine the ground and excited state wavefunctions and energies. On the other hand, numerical or analytical energy derivative techniques have also been used for push–pull systems. Among these techniques is the coupled perturbed Hartree–Fock procedure (CPHF) [16] which provides coupled Hartree–Fock (CHF) values [17–20]. Numerical procedures which consist in applying a finite difference expression to obtain β have been used mainly at the Hartree–Fock and the second-order Møller–Plesset perturbation theory levels [21,22]. Whereas derivative techniques have mostly been employed at the ab initio level, the wavefunctions and energies entering in the SOS β expressions are often computed within semi-empirical schemes.

In this paper we study push–pull systems based on a polymethineimine (PMI) segment. PMI has a backbone constructed by the alternation of carbon and nitrogen atoms; it is also sometimes named polycarbonitrile or polynitrile. PMI chains which are isoelectronic to polyacetylene (PA) chains were synthesized by Wöhrle 25 years ago [23,24]. Recently, Albert et al. [25] computed, using a Pariser–Parr–Pople Hamiltonian, the β values for small all-*trans* PMI oligomers ranging from $C_2N_2H_4$ to $C_5N_4H_7$. They determined the chain length dependence expression: $\beta = cN^{3.4}$, where N is the number of carbon atoms and c is a constant.

Our interest is oriented towards the evaluation of the first hyperpolarizability of stereoregular polymers. Since most of the infinite systems have an inversion centre, the first hyperpolarizability of stereoregular polymers is often zero, and only a few works have investigated the calculation of β in

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one-dimensional periodic systems. The behaviour of the first hyperpolarizability per unit cell versus the number of unit cells of increasingly large PMI oligomers was previously described and explained within Hückel [26], Pariser–Parr–Pople [27] and ab initio [28] schemes. Fig. 1 shows the longitudinal first hyperpolarizability per unit cell obtained at the CHF/6-31G level for increasingly large PMI chains. The shape of the curve, especially the presence of a maximum, has been rationalized in terms of the interplay between delocalization and asymmetry effects [26–28]. Indeed, when the chain is growing the electron delocalization along the backbone increases, thus giving an increasing contribution to the first hyperpolarizability, but simultaneously the chain is becoming more and more centro-symmetric, which leads to a decreasing contribution to the first hyperpolarizability. The presence of the maximum was explained via a simplified SOS model [27]; however, it was shown that the frequently used two-level model was inadequate to reproduce the first hyperpolarizability of extended PMI oligomers. The effects of bond alternation [26–28], nuclear alternation [26] and method of calculation (coupled versus uncoupled Hartree–Fock schemes) [27,28] on the shape of the curve have previously been investigated. We have demonstrated that the more conjugated the chain, the larger the first hyperpolarizability value at the maximum, the larger the chain for which this maximum is reached, the larger the fall-off towards the asymptotic value, but the slower the saturation.

As described previously, the $\Delta\beta_{zzz}$ sign change (see Fig. 1, z is the longitudinal direction) is related to the relative and opposed asymmetry effects due to the chain ends and the unit cells. Consequently, by using various donor and acceptor groups one expects not only a variation of the β_{zzz} amplitude but also sign changes. An interesting point thus consists of the investigation of these push–pull PMI chains and of their potentials as systems presenting large NLO responses. In particular, the comparison with the parent push–pull polyenes brings further characterization of the PMI systems. Since we desire to assess the electronic effects generated by the donor–acceptor groups on the different conjugated segments, we do not consider the donor–acceptor-induced geometrical modifications. We thus focus restrictively on the effects of the substitution of carbon atoms by nitrogen atoms on the β values. We call the compounds built from the –(CH=CH)– units, PA-type; those with the –(CH=N)– units, PMI-type.

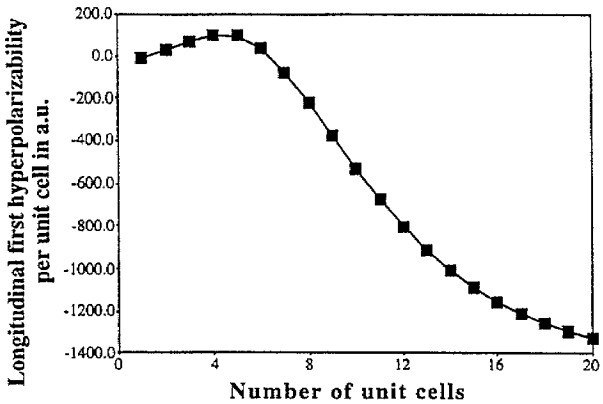

Fig. 1. Longitudinal first hyperpolarizability per unit cell in a.u. $(\beta_{zzz}(N)-\beta_{zzz}(N-1))$ for PMI stereoregular chains within the CHF/6-31G scheme; 1.0 a.u. of first hyperpolarizability $=3.206\times10^{-53}$ C^3 m^3 $J^{-2}=8.641\times10^{-33}$ e.s.u.

Original β studies of donor–acceptor systems with a conjugated segment built from carbon and nitrogen atoms have been carried out by Tsunekawa and Yamaguchi [19,20] and are summarized in the review article of Kanis et al. [3]. In this CHF ab initio work concerned with the substitution of carbon by nitrogen atoms, they showed that β decreases with the number of nitrogen atoms introduced into the π-conjugated segment. Their study, carried out for the α,ω-nitro-amino-substituted backbone which contains up to three nitrogen and three carbon atoms, also discussed the variation of β as a function of the nitrogen position along the backbone. They explained qualitatively these β trends by a study of the frontier orbitals: when introducing nitrogen into the chain the energy of the HOMO level is lowered and the gap between HOMO and LUMO level is enlarged. They demonstrated the good correlation between the energy gap value and the β amplitude. By studying the orbital coefficients of the HOMO and LUMO for O_2N–CH=N–NH_2 and O_2N–N=CH–NH_2, they showed that the induced polarization by the mixing of HOMO and LUMO is larger in the first than in the second, which explains the larger β value.

Section 2 presents the methodology employed as well as the geometries used. Section 3 describes the results obtained and their interpretation. In Section 4 we conclude and summarize.

2. Method of calculations

The application of a static uniform electric field $\vec{E}$ on a system leads to a reorganization of its charge distribution. This reorganization is often characterized by representing the dipole moment as a power series in $\vec{E}$ [1,2,29]:

$$\vec{\mu}=\vec{\mu}_0+\overleftrightarrow{\alpha}\cdot\vec{E}+\frac{1}{2}\overleftrightarrow{\beta}:\vec{E}\vec{E}+\frac{1}{6}\overleftrightarrow{\gamma}:\vec{E}\vec{E}\vec{E}+\cdots \quad (1)$$

where $\overleftrightarrow{\alpha}$ is the electric dipole polarizability tensor which represents the linear response of the dipole moment to the external electric field. $\overleftrightarrow{\beta}$ and $\overleftrightarrow{\gamma}$ are the first and second hyperpolarizabilities. Vibrational contribution to some NLO processes could be substantial [30–33] for molecules and polymers, but firstly we restrict our study to the electronic component of the polarizability and first hyperpolarizability. In addition, we only consider static electric field, thus computing only the static polarizability and first hyperpolarizability. Since the UCHF scheme fails to reproduce the CHF β values for large PMI chains, we adopt the CHF scheme which includes the field-induced electron reorganizational effects. These CHF values can be obtained either via the numerical Hartree–Fock finite field method [34], via the random phase approximation [35], or via the analytical CPHF iterative

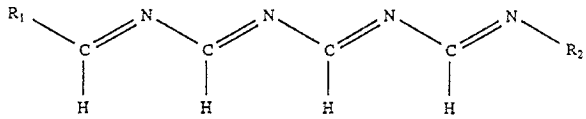

Fig. 2. Sketch of a push–pull system based on the PMI segment containing four unit cells.

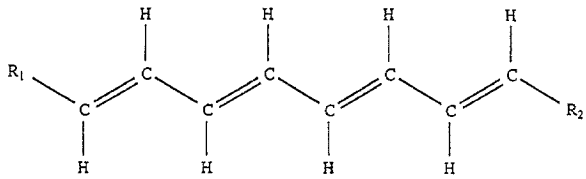

Fig. 3. Sketch of a push–pull system based on the PA segment containing four unit cells.

derivative scheme [16]. We employ the HONDO 95.3 program which relies on the latter [36]. The split-valence 6-31G atomic basis set [37] has been chosen for its adequateness in evaluating α and γ of PA chains [38], as well as β of push–pull systems [3].

The geometrical structures of the planar oligomers (see Figs. 2 and 3) were constructed by taking as a building block the central unit cell of $C_8N_8H_{11}$ (8-unit cell PMI oligomer) optimized with the 6-31G basis set. Thus, the following parameters have been used for the unit cell of the backbone: $d_{C=N}=1.264$ Å, $d_{N-C}=1.390$ Å, $d_{C-H}=1.088$ Å, $\alpha_{N-C=N}=120.2°$ and $\alpha_{N-C-H}=118.3°$. For the bond length and angle values of the R_1 and R_2 side groups standard parameters have been chosen. The oligomers based on a carbon backbone (PA-type, Fig. 3) have the same geometry specification as the PMI-type systems; showing the bond length alternation of PMI and not of PA. In this way, we will determine specifically the effects due to the donor–acceptor groups on the different conjugated segments.

We choose the following end groups: NO_2, H, F, OH, NH_2 and make all the possible combinations between them. Therefore we study sometimes donor–donor systems.

The systems considered here have a one-dimensional extension and we focus then on the longitudinal components of the polarizability (α_{zz}) and the first hyperpolarizability (β_{zzz}). Indeed, as the delocalization along the backbone is larger than in the perpendicular and transverse direction, the α_{zz} and β_{zzz} components are, by far, the most interesting to enhance.

3. Results and discussion

3.1. Study of different donor–acceptor groups

In Table 1 we present the CHF/6-31G α_{zz} and β_{zzz} values for the various push–pull components considered. PA-based push–pull systems see their first hyperpolarizability values changing sign, but not amplitude, when switching the two end groups (R_1 and R_2) because the backbone $-(CH{=}CH)_4-$ is centro-symmetric. It is not the case for

Table 1
CHF/6-31G longitudinal polarizability and first hyperpolarizability (in a.u.) of different push–pull systems based on PA or PMI conjugated segments

R_1	R_2	R_1–$(CH{=}CH)_4$–R_2		R_1–$(CH{=}N)_4$–R_2	
		α_{zz}	β_{zzz}	α_{zz}	β_{zzz}
NO_2	NH_2	318.1	8330.3	294.7	7598.2
NH_2	NO_2	318.1	−8330.3	278.2	−3446.3
NO_2	OH	288.8	6526.3	263.2	5650.9
OH	NO_2	288.8	−6526.3	249.5	−2501.0
NO_2	F	284.6	5083.6	226.2	2731.6
F	NO_2	284.6	−5083.6	234.8	−1714.3
NO_2	H	281.6	3826.9	222.9	1845.4
H	NO_2	281.6	−3826.9	237.2	−1126.5
H	NH_2	225.8	1937.4	224.4	2337.9
NH_2	H	225.8	−1937.4	205.9	−963.2
H	OH	206.6	1409.7	201.7	1715.9
OH	H	206.6	−1409.7	182.7	−638.8
F	NH_2	216.4	1109.9	214.6	1495.5
NH_2	F	216.4	−1109.9	204.3	−456.6
F	OH	198.4	707.5	193.1	1038.0
OH	F	198.4	−707.5	181.1	−198.8
H	F	190.5	611.4	179.2	683.5
F	H	190.5	−611.4	174.0	−251.1
NH_2	OH	227.8	65.1	222.6	434.0
OH	NH_2	227.8	−65.1	219.4	824.2
H	H	194.7	0.0	179.2	182.2

PMI-type systems. The values, in Table 1, are ordered according to the β_{zzz} magnitude of the PA-type chains.

Concerning α_{zz}, the now well-known trends are observed. (1) The more conjugated the system, the larger is α_{zz}. This explains why the PA-type molecules have larger α_{zz} values than the corresponding PMI-type compounds. (2) The more extended the chain, the larger is α_{zz}; the addition of large end groups also leads to an increase of α_{zz}. Moreover, one can notice that PMI-type systems present a different polarizability value when the end groups are placed either at the C end (R_1) or at the N end (R_2). In order to obtain the largest polarizability one should place the donor at the N end, and, if there is only one acceptor group, it must also be added at the N end.

The trend for β_{zzz} is more complicated due to the numerous factors influencing the final result. For both PA-type and PMI-type systems, one can verify that β obtained for a system with a donor and an acceptor group is larger than the sum of the β obtained when placing alone either the acceptor or the donor group. For the PA-type systems, β_{zzz} is, as expected, larger when increasing the push–pull strength; the very strong acceptor group NO_2 giving the enhanced-β compounds. The push–pull system with a nitro and an amino group leads to the largest β_{zzz} value. Putting a weak donor and strong acceptor group (F and NO_2 $\beta_{zzz}=5083.62$) leads to a response two orders of magnitude large than with two donor groups (NH_2 and OH: $\beta_{zzz}=65.08$). For the PMI-type compounds the observations are the following: (1) The β_{zzz} values are ordered mostly in the same way as for the PA-type compounds and are significantly larger than the values obtained

for PMI oligomers (where $R_1 = R_2 = H$). (2) If we switch the two end groups β_{zzz} not only changes sign (except for NH_2–$(CH{=}N)_4$–OH) but its magnitude changes by a factor of two or three. Moreover, $|\beta_{zzz}|$ is the largest when the strongest acceptor is placed at the C end. (3) For weak push–pull substituents the β_{zzz} amplitudes of PMI-type systems are larger than the β_{zzz} values of the corresponding PA-type compounds. The explanations are as follows: (1) For strong push–pull systems, unlike non-substituted PMI oligomers, β_{zzz} is principally due to the presence of the donor and acceptor groups and not to the existence of an asymmetric unit cell, which explains that the small delocalization and asymmetry effects induced by the replacement of C by N do not affect the ordering of the β_{zzz} values. (2) In PMI chains, the polarity of the chain (which is linked to β) has two components: the unit cells and the end groups; the latter component being the more important when dealing with strong acceptor and donor groups. Moreover, these two components are non-additive. When placing an acceptor group at the C end (R_1) and a donor group at the N end (R_2), the two polarity components have the same sign: a large positive β_{zzz} value is observed. If one switches the two end groups, the two polarities have opposite directions: a smaller negative β_{zzz} value is obtained. (3) As explained in our previous papers and summarized in the Introduction, the two main parameters which influence the first hyperpolarizability are the delocalization and the asymmetry, this last parameter coming from two parts in a finite chain: the chain ends and the unit cell. One of these two parameters is always a limiting factor for the first hyperpolarizability. When dealing with strong push–pull systems, the delocalization along the backbone is the limiting factor in comparison with the asymmetry and therefore PA-type structures provide the largest β_{zzz}. On the other hand, for compounds having weak donor and acceptor groups, the delocalization along the backbone is less crucial than the asymmetry, leading to larger β_{zzz} for the PMI-type systems when both unit cells and the end groups present parallel polarization. Our results corroborate well the study of Tsunekawa and Yamaguchi [19,20]. We also obtain a good correlation between the optical gap and the β_{zzz} values.

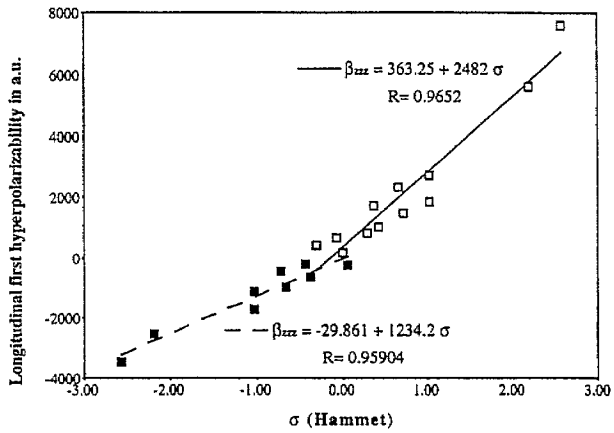

Fig. 4. CHF/6-31G longitudinal first hyperpolarizability vs. the Hammet σ parameters for PMI-type oligomers. R is the correlation coefficient.

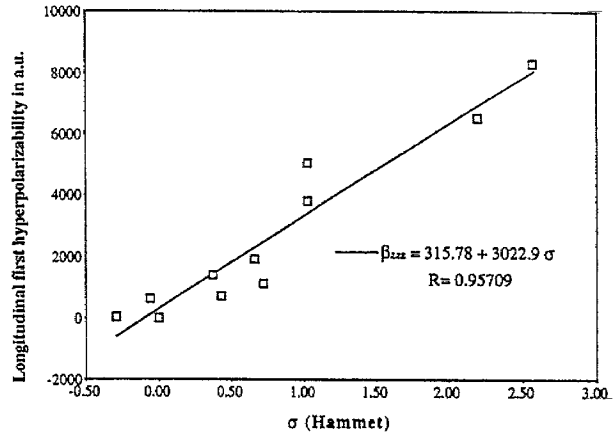

Fig. 5. CHF/6-31G longitudinal first hyperpolarizability vs. the Hammet σ parameters for PA-type oligomers. R is the correlation coefficient.

In order to quantify the susceptibility of the conjugated segment which respect to the first hyperpolarizability, on Figs. 4 and 5 are drawn the graphs of β_{zzz} versus the Hammet σ parameters [39]. Two sets of σ parameters are currently used, the first (σ_0) for systems with weak donor and acceptor groups, the second (σ_+/σ_-) for compounds having strong donors and acceptors. As described in [39] numerous sets of parameters should exist between these two limits. We have used the σ_0 set for all the compounds except for α,ω-nitro-amino and α,ω-nitro-hydroxy systems where the σ_+/σ_- set was used. For PMI-type systems β_{zzz} values have been separated into two groups to take into account the influence of the switch between R_1 and R_2. It can be seen that a nearly linear relation exists between the σ and β_{zzz} values; the slope of the line giving the susceptibility of the backbone with respect to the first hyperpolarizability. Since the susceptibility is linked to the delocalization along the backbone, the susceptibility is larger for PA-type than for PMI-type compounds. In this last case, the susceptibility is larger when the polarities of both the unit cell and the push–pull pair are parallel.

3.2. Study of the chain length dependence

We calculate the evolution with chain length of the first hyperpolarizability per unit cell for the α,ω-nitro-amino PMI homologous series (O_2N–$(CH{=}N)_N$–NH_2) with N ranging from 1 to 10. We use the following formula:

$$\Delta\beta_{zzz}(N) = \beta_{zzz}(N) - \beta_{zzz}(N-1) \quad (2)$$

where N is the number of unit cells, to determine the first hyperpolarizability per unit cell ($\Delta\beta_{zzz}(N)$). Fig. 6 shows the comparison between the PMI and α,ω-nitro-amino PMI chains. The shapes of the two curves are similar: presenting a maximum for four unit cells, but the substituted PMI chains present, at the maximum, a $\Delta\beta_{zzz}$ value about 35 times larger than the non-substituted PMI chains. The fall-off towards the

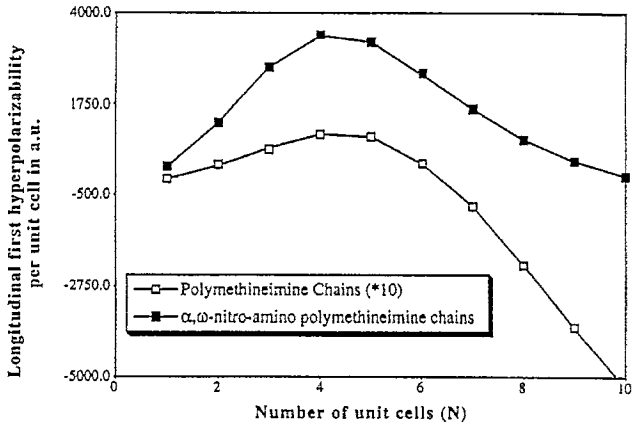

Fig. 6. CHF/6-31G longitudinal first hyperpolarizability per unit cell vs. the number of unit cells for PMI and α,ω-amino-nitro PMI chains. The values for PMI oligomers have been multiplied by 10.

asymptotic polymeric value is more rapid for non-substituted chains. Explanations for this 'dromedary-back' shape were given in our previous papers [26–28]. The longest α,ω-nitro-amino PMI oligomers considered are still too short to address the asymptotic behaviour $\Delta\beta_{zzz}$.

4. Conclusions and outlook

We have examined donor–acceptor systems of which the asymmetric conjugated segment is built from the alternation of carbon and nitrogen atoms. In order to maximize the β_{zzz} value, selecting an asymmetric segment is only useful when dealing with systems having weak push–pull substituents. This has been explained by the interplay between delocalization and asymmetry effects. The existence of a maximum for the curve of β_{zzz} versus the number of unit cells for α,ω-nitro-amino PMI chains has been shown. This maximum is reached, as in the case of non-substituted PMI chains, for a chain containing four unit cells, but the $\Delta\beta_{zzz}$ at that maximum is 35 times larger than for PMI chains.

However, the combination of calculations with other donor–acceptor pairs and with longer conjugated segments will further address the effects of the balance between the asymmetry (of the unit cell and the chain ends) and the electron delocalization. Geometrical effects also deserve to be investigated.

Dedication

This contribution is dedicated to Professor Alan J. Heeger on the occasion of his 60th birthday.

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