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Møller–Plesset evaluation of the static first hyperpolarizability of polymethineimine

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Abstract

A finite oligomer approach is used to compute the longitudinal component of the static electronic first-hyperpolarizability per unit cell ($\Delta\beta_L(N)$) of polymethineimine. The longitudinal first hyperpolarizability (β_L) is calculated accounting for electron correlation effects via the Møller–Plesset partitioning. The influences of the basis set size, of the order in electron–electron interactions up to which the electron correlation effects are accounted for and of the modification of the equilibrium geometry due to the inclusion of electron correlation are considered. Contrary to the Hartree–Fock level for which $\Delta\beta_L(N)$ vs. N firstly presents a minimum then increases towards its polymeric value, at the MP2 level, $\Delta\beta_L(N)$ evolves monotonically with chain length and its asymptotic value is 7.7 times larger than the CPHF results reaching the large value of 4.2×10^{-30} esu g⁻¹ mol. © 1998 Elsevier Science B.V.

1. Introduction

Polymethineimine (PMI), H–(CH=N)_N–H, possesses a potential for second-order non-linear optics (NLO) applications [1–3]. This polymer, synthesized in the 1970s [4,5], has a structure similar to polyacetylene (PA) but half of the carbon atoms are replaced by nitrogen atoms. PMI chains present thus an attractive combination of π -electron conjugation and push–pull effects, i.e. of delocalization and asymmetry. The asymmetry (and β_L) in the finite oligomers originates from the chain ends and the unit cells, this last contribution being the only one in the polymer

[2]. At the Hartree–Fock (HF) level, the interplay between these two contributions leads, for the longitudinal electronic static first-hyperpolarizability per unit cell ($\Delta\beta_L(N) = \beta_L(N) - \beta_L(N-1)$, N being the number of unit cells), to a minimum for small chain length, a change of sign at medium chain length and then a saturation to the polymeric limit [2,3]³. The aim of this Letter is to compute, by including the electron correlation (EC) effects, $\Delta\beta_L(N)$ of the PMI oligomers and to extrapolate to the polymer ($N \rightarrow \infty$). Two strategies are currently available. The first consists in the development and implementation of polymeric techniques able to compute the NLO properties of the infinite chain

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³ With respect to our previous investigations, the chains are oriented in the opposite direction, i.e. –N=CH–N=CH–, in such a way that μ_{0L} and β_L are positive for large oligomers.

directly by taking advantage of the translational symmetry of the polymer. Some progress has been achieved towards the evaluation of the polymer (hyper)polarizabilities [6–8], but EC effects of the hyperpolarizabilities are still restricted to molecular systems [9,10]. We are left with the second strategy consisting of computing the first hyperpolarizability (β_L) of increasingly large oligomers, in calculating the value by unit cell and in extrapolating to the infinite chain length.

In general, EC has a large impact on the NLO properties of molecules [9,10] and polymers [11–14]. EC affects the NLO properties in two ways. On one hand, EC changes the electronic structure and has a *direct* impact on β_L , whereas, on the other hand, the modification of the equilibrium geometry has an *indirect* effect on β_L . Both contributions have been shown to be important for the second hyperpolarizability (γ) of conjugated polymers [13]. The difficulty is to reach saturation for $\Delta\beta_L(N)$ when EC is included because EC techniques are more CPU time demanding than the HF scheme. The common strategy to circumvent this difficulty is to compute the ratio between the correlated and uncorrelated (hyper) polarizabilities which generally converges faster than any of its components [11–14].

After a brief description of the methods which are used to compute β_L , we present the results and their interpretations. We investigate the effects of basis set size as well as the level of inclusion of the EC and we detail both its *direct* and *indirect* contributions to $\Delta\beta_L(\infty)$. In order to obtain a quantitative evaluation in terms of asymmetries and electronic delocalization, the β_L/N curves are fitted to a function which has recently been proposed [2]. Finally, we draw conclusions.

2. Methodology

First, each oligomer has been fully optimized with the 6-31G basis within the HF or the second-order Møller–Plesset (MP2) schemes. We consider, here, all-trans PMI chains which are slightly bent. Then we compute β_L of each oligomer, as explained below.

The application of a static uniform electric field \vec{E} on a molecule leads to a reorganization of its nuclear

and electronic distributions and, subsequently a modification of its energy (ϵ). This variation is represented by a Taylor series in \vec{E} :

$$\epsilon = \epsilon_0 - \vec{\mu}_0 \cdot \vec{E} - \frac{1}{2!} \vec{\alpha} : \vec{E}\vec{E} - \frac{1}{3!} \vec{\beta} : \vec{E}\vec{E}\vec{E} - \dots, \quad (1)$$

where ϵ_0 and $\vec{\mu}_0$ are the energy and the dipole moment, respectively, of the molecule in the absence of \vec{E} . $\vec{\alpha}$ and $\vec{\beta}$ are the electric dipole polarizability and first hyperpolarizability tensors, respectively. Due to the large π -electron delocalization along their backbone, PMI chains present the largest component of the β tensor in the longitudinal direction [2]. We have therefore restricted our study to the longitudinal component of β : β_L .

The β_L values of the various oligomers have been computed by adopting the numerical finite field (FF) method:

$$\beta_L^{0,k} = \lim_{E_L \rightarrow 0} \left[\epsilon(-2^{k+1}E_L) - 2\epsilon(-2^kE_L) + 2\epsilon(2^kE_L) - \epsilon(2^{k+1}E_L) \right] \left[2(2^kE_L)^3 \right]^{-1}, \quad (2)$$

where the basic external electric field amplitude, $E_L = 2 \times 10^{-4}$ au (1 au of electric field = 5.1422×10^{11} V m⁻¹). k ($k = 0, 1, 2, 3, 4, 5$ and 6) defines the lowest field amplitude used. The field amplitudes follow a power of two pattern to ease Romberg's procedure [15] which improves the accuracy (see Ref. [16] for more details). The SCF convergence criterion has been tightened to 10^{-13} au in the Gaussian94 program [17]. Such a tightened threshold and well-chosen external electric field amplitudes are necessary to reach sufficient accuracy on the β_L values. As, at the HF level, analytic β_L values can be computed by the coupled perturbed Hartree–Fock (CPHF) method [18], a comparison between FF-HF and CPHF β_L provides an interesting insight into the numerical accuracy of the finite-difference procedure. We used the Gaussian94 and Hondo95.3 [19] program to compute the CPHF β_L of each molecule. In our case the deviations observed between CPHF and FF-HF are, for the largest oligomers, around 1 au.

β_L is computed with the 6-31G atomic basis set

[20], which is well known to give good (hyper)polarizabilities estimations for large molecules [21,22]. The EC is considered in the framework of the Møller–Plesset (MP) partitioning scheme which fulfills the size-consistency criterion. Moreover, at its simplest level (MP2), it presents an attractive balance between accuracy and computational cost.

3. Results and discussion

In Table 1 we show the ratios between the MP2 β_L obtained with the 6-31G basis and the Hurst et al. 6-31G + pd basis [22] designed to reproduce accurately experimental values of γ . Hurst et al. worked on polyacetylene chains and gave no exponent for the p and d diffuse functions added on nitrogen atoms. We have chosen an exponent of 0.0715 to be consistent with the ratio between the C and N exponents of the Sadlej basis [23]. By adopting a method based on three different fitting functions [2] an extrapolated 6-31G + pd/6-31G ratio close to one, is obtained for the MP2 β_L . The 6-31G basis set seems therefore sufficient to carry out further investigations on the PMI oligomers.

Together with the problem of the basis set, comes the question of the EC technique used. How far should the EC be included to obtain ‘correct’ β_L values? Our previous work on small oligomers [24] has shown that including the third- and fourth-order corrections within the MP scheme significantly changes β_L . The results of the MP2, MP3 and MP4 calculations on oligomers containing up to 5 unit cells, displayed at Table 2, partially confirm this statement. The MP3 scheme gives larger β_L than the MP2 and the MP4 techniques, and should thus be left on the side. Obviously the MP4/MP2 ratio increases slightly with chain length and is geometry sensitive; the fourth-order correction being larger for the MP2 geometry. The different components of the total MP4 correction can be evaluated separately. For the pentamer (MP2 geometry) the relative contributions to the MP4 correction to β_L are: 127% for the singles, –100% for the doubles, 63% for the triples and 10% for the quadruples. The triples are thus essential to obtain a correctly balanced MP4 correction. The chains used are too small to extrapolate this MP4/MP2 ratio to the polymer limit. However, we

Table 1

β_L (MP2/6-31G + pd)/ β_L (MP2/6-31G) ratio as a function of the number of unit cells, N , of the all-trans PMI chains

N	Ratio
1	1.564
2	1.228
3	1.146
4	1.106
5	1.079
6	1.059
∞	0.991 ± 0.48

All results have been obtained at the MP2/6-31G geometry.

notice that the magnitude of the higher-order corrections decreases with chain length. With respect to the investigation of γ_L of PA chains done by Toto et al. [11] our MP4/MP2 ratio is smaller, more sensitive to the geometry and to the size of the chain.

The β_L obtained by the CPHF and FF-MP2 calculations done on oligomers going up to the icosamer are displayed in Table 3. For the HF geometry the evolution with chain length of $\Delta\beta_L(N)$ is displayed at Fig. 1. Obviously the main qualitative difference between the MP2 and HF $\Delta\beta_L(N)$ is the fact that, at MP2 level, no minimum is found for small chains and no change of sign occurs. In other words, at the MP2 level, the dipole moment and the first hyperpolarizability are always parallel whereas, with the CPHF technique, it is only the case for large chains ($N \geq 8$). From our previous observations [2,3], we deduce that the HF level is biased towards the chain end contribution, i.e. it underestimates the unit cell contribution. The MP2 value for the polymer is much larger than the HF one. As the HF and MP2 β_L are different for small and medium chain lengths, there is no reason to hope that the MP2/HF ratio converges fast. Indeed, it is not saturating faster than the MP2 or HF β_L taken alone. We thus compute the MP2 β_L until the saturation is sufficient to extrapolate the polymeric value with a suitable accuracy. A size of 20 unit cells satisfies this criterion. Using our extrapolation procedure [2] with a stability criterion of 1%, we obtain the FF-MP2 and CPHF $\Delta\beta_L(\infty)$ to be 8413 ± 204 and 1693 ± 70 au, respectively. The *direct* effect of EC is thus an increase of the polymeric $\Delta\beta_L$ by a factor of 5.

To estimate the *indirect* effect of EC we have

Table 2

 β_L of all-trans PMI oligomers in au: comparison between the different MP techniques

N	HF geometry			MP2 geometry		
	MP2	MP3/MP2	MP4/MP2	MP2	MP3/MP2	MP4/MP2
1	10.7	1.251	0.511	17.1	1.206	0.535
2	112.1	1.061	0.663	155.2	1.069	0.582
3	438.8	1.051	0.716	615.1	1.058	0.624
4	1129.8	1.053	0.750	1630.5	1.060	0.656
5	2320.6	1.049	0.780	3437.2	1.056	0.688

All results have been obtained using the 6-31G basis set and at the HF/6-31G or MP2/6-31G geometries. N is the number of unit cells. (1 au of first hyperpolarizability = 3.2063×10^{-53} C³ m³ J⁻² = 8.641×10^{-33} esu).

fully optimized the geometry of the PMI oligomers up to the dodecamer at the MP2/6-31G level. In comparison with the HF equilibrium geometries, the MP2 ones present longer single and double bonds but a smaller bond length alternation ($\Delta r = d_{N-C} - d_{C=N}$). Indeed, in the case of the dodecamer, Δr at the center of the chain is 0.1207 Å (0.1093 Å) for the HF(MP2) geometries. This decrease of Δr leads to a smaller asymmetry and to a larger delocalization along the backbone, which, in principle, can lead to a decrease or increase of β_L . β_L increases in this case. The dodecamer is too small to permit an estimate of $\Delta\beta_L(\infty)$. To circumvent this problem, we computed the ratio between the FF-MP2 β_L obtained with the MP2 and HF geometries (see Fig. 2). This ratio is remarkably stable when chain length is increasing and tends towards a value close to 1.55. Similarly, for PA chains, an increase of 50% of γ_L was calculated when shifting from HF to MP2 geometry [11]. Combination of both the *direct* and *indirect* component of EC estimated at the MP2 level provides us with a $\Delta\beta_L(\infty)$ of $(8413 \pm 204) \times (1.55 \pm 0.01) = 13040 \pm 327$ au, much larger than the CPHF value of 1693 au.

In order to fit the global behavior with chain length of β_L per unit cell and to evaluate the relative importance of the chain ends vs. backbone asymmetry contributions, we use the expression [2,3]:

$$\frac{\beta_L}{N} = \left[m_1 + m_2 \tanh\left(\frac{N - m_3}{m_4}\right) \right] \left(1 + \frac{m_5}{N} \right), \quad (3)$$

where $[m_1 + m_2 \tanh((N - m_3)/m_4)]$ is a delocalization function, and $(1 + m_5/N)$ is an asymmetry function. The asymmetry function is the sum of the contributions originating from the backbone (= 1)

and from the chain ends ($= m_5/N$). In the delocalization, function the inflection point occurs at $N = m_3$. m_2 is the magnitude of the change in β_L/N from $N = m_3$ to $N = \infty$ and m_1 is the rate of this change. We refer the reader to Ref. [2] for an extensive discussion of this fitting function.

The results of this by, fitting procedure using

Table 3

 β_L in au of the all-trans PMI with the 6-31G atomic basis set

N	HF geometry		MP2 geometry	
	CPHF	FF-MP2	CPHF	FF-MP2
1	4	11	-3	17
2	-26	112	-31	155
3	-73	439	-109	615
4	-146	1130	-254	1631
5	-215	2321	-440	3437
6	-236	4118	-604	6219
7	-160	6584	-668	10083
8	48	9751	-568	15059
9	411	13609	-261	21111
10	936	18123	271	28155
11	1621	23241	1022	36084
12	2458	28903	1977	44771
13	3432	35044		
14	4527	41595		
15	5728	48496		
16	7021	55688		
17	8391	63124		
18	9825	70756		
19	11313	78541		
20	12843	86422		

$\Delta\beta_L(\infty)$ 1693 ± 70 8413 ± 204 2878 ± 207 13040 ± 327

The HF (MP2) values have been computed by the CPHF (FF) procedure. At the bottom of the table, the extrapolated values per unit cell are displayed. See the text for more details about the extrapolation procedures.

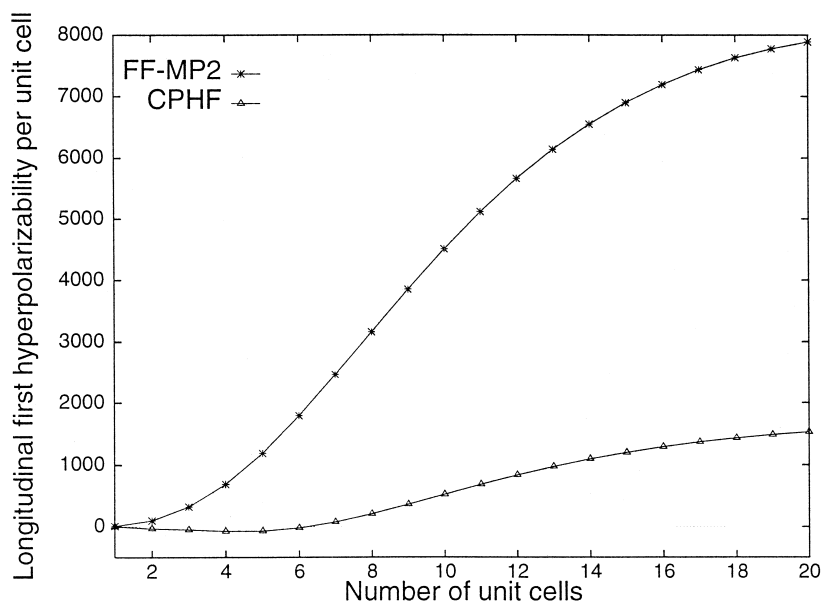


Fig. 1. CPHF and FF-MP2 $\Delta\beta_L(N)$ (au) of all-trans PMI chains as a function of the number of unit cells (N). These results have been obtained on the HF/6-31G equilibrium geometry with the 6-31G basis set.

points ranging from $N = 2$ to $N = 12$ are displayed in Table 4. At the HF geometry, fittings realized with points going up to $N = 20$ do not lead to

significant variations. Obviously the FF-MP2 results differ from the CPHF ones by the larger m_1 and m_2 and smaller $|m_5|$. This is consistent with the larger

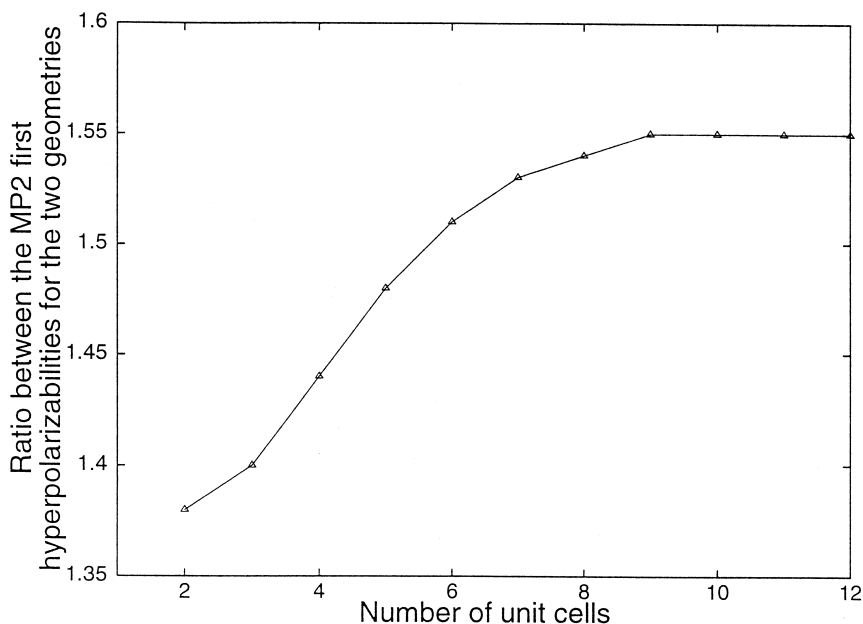


Fig. 2. Ratio of FF-MP2 β_L obtained with the MP2 and HF equilibrium geometries for all-trans PMI oligomers.

Table 4
Least-squares fitting parameters obtained with Eq. (3)

Method	Geometry	$m_1 + m_2$	m_2	m_3	m_4	m_5
CPHF	HF	1213	632	12.0	6.4	−7.7
	MP2	2017	1038	12.6	6.1	−9.7
FF-MP2	HF	4323	2385	9.6	7.4	−1.2
	MP2	6798	3791	9.5	7.5	−1.4

$m_1 + m_2$ and m_2 have dimension of β and are given in au while all other quantities are pure numbers. All results have been obtained with the 6-31G basis set.

$\Delta\beta_L(N)$ and the absence of a minimum in the MP2 curves: at the MP2 level the contribution of the chain ends to $\Delta\beta_L(N)$ is 7 times smaller than at the HF one. When shifting from the HF to MP2 geometry, the delocalization increases and the asymmetry of the unit cell decreases (because single and double bonds present closer length). Indeed, m_1 , m_2 and $|m_5|$ are larger. The FF-MP2 ratio between the $m_1 + m_2$ values obtained for the two geometries is 1.57, in good agreement with the 1.55 value found above. The corresponding CPHF ratio is 1.7, this allows us to estimate the CPHF $\Delta\beta_L(\infty)$ of $(1693 \pm 70) \times (1.7 \pm 0.1) = 2878 \pm 207$ au for an MP2 equilibrium geometry.

4. Conclusions and outlooks

The $\Delta\beta_L(\infty)$ of PMI chains has been investigated by taking into account the effect of EC at the MP2/6-31G level. In comparison with the CPHF value, $\Delta\beta_L(\infty)$ has been shown to be multiplied by 7.70 (4.97×1.55 , combination of both the *direct* and *indirect* effects of EC) to reach 112.7×10^{-30} esu. However, this large value is, probably, overestimated considering the large MP4 correction obtained for small oligomers. This factor of 7.70 has to be compared with a factor of 1.58 for β_L of *p*-nitroaniline [25] or a factor of 2.84 for γ_L of polyacetylene [11].

This investigation points out that PMI deserves further theoretical and experimental attention. Indeed, our best estimation for the $\Delta\beta_L(\infty)$, 13040 au, corresponds, reported with respect to the molecular weight of the unit cell, to 4.2×10^{-30} esu g^{−1} mol. This value looks attractive in comparison to the one

of standard push–pull systems. Indeed the experimental value for 4-(dimethylamino)-4'-nitrostilbene is $0.3(1.7) \times 10^{-30}$ esu g^{−1} mol at a wavelength of 1910 (1064) nm [21].

To complete the present study, the investigation of the frequency dependence and the calculation of the vibrational contribution to the β_L would be interesting [26].

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