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# Molecular Nonlinear Optical Parameters of π-Conjugated Nonalternant Hydrocarbons Obtained in Semiempirical Local Coupled-Cluster Theory

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ABSTRACT: The π-electron dipole polarizabilities and hyperpolarizabilities of organic conjugated hydrocarbons with odd-membered carbon cycles (nonalternant systems) are calculated using local semiempirical coupled-cluster theory. The peculiarity of the approach is the use of local ethylene π-molecular orbitals to represent double bonds in the molecule (cue-CCSD approach). The size-limit values of the (hyper)polarizabilities for different types of nonalternant oligomers obtained in the calculations show a significant dependence on the molecular structure. The effect of the electron correlation in the hyperpolarizability calculations is investigated using different levels of the coupled-cluster method including the simplest CCSD model and other models up to the model where the correlation effects due to all four electron excitations are accounted for, as well as with the full configuration interaction model.
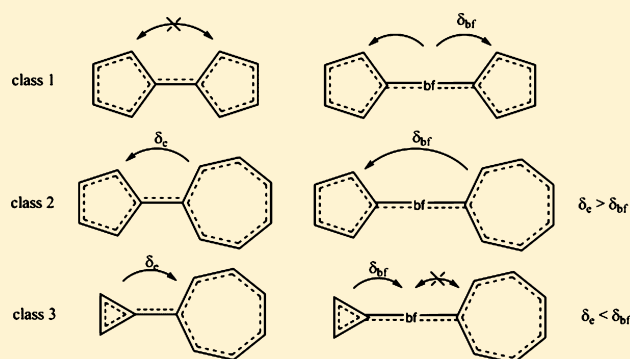
1. INTRODUCTION

The expanding field of optical devices requires fabrication of new materials with properties which are better suited for the new applications these devices are expected to provide.[1−3] These properties include certain electro-optical effects which can be characterized by the electro-optical parameters of the molecular systems forming the new materials. Among them the polarizability, hyperpolarizability, absorption wavelength, scattering coefficient, etc. are the most important.

When a new optical device is designed, it is often necessary to search through a large number of existing materials or to synthesize new ones to obtain the specific properties meeting the device specifications. Therefore, without an effective approach, which can be used to predict optical properties of the material being considered for a specific application, finding a suitable material may require significant resources. As computational experience shows, an analysis based on a pure phenomenological quantity—structure activity relationship (QSAR) or some other empirical scheme is usually insufficient to correctly estimate the optical parameters of such materials as polymers, which are often used in optical applications. However, it should be mentioned that some progress has been recently achieved in employing QSAR-based approaches to predict the optical properties of *compact* (nonpolymeric) molecules.[4]

Recent progress in *ab initio* methodologies and the increasing power of modern computers have enabled fairly accurate quantum-chemical description of various linear and nonlinear optical parameters of many organic molecules. Calculations performed with the use of *ab initio* methods with adequate basis sets which include polarization and diffuse functions and an accurate accounting for the electron correlation have provided very good predictions of the optical properties. Among the methods where the account of the correlation effects is particularly accurate, coupled cluster (CC) methods are the most effective.[5−7] The results obtained in calculations performed with CC techniques are for most systems very close to the available experimental data. However CC methods can only be applied to relatively small systems because of their high computational cost.

An alternative approach to predict optical properties of materials in the calculations is to employ semiempirical methods which can be used to describe larger molecular systems (oligomers of conjugated polymers, supramolecular structures, etc.). However, also in those methods the accuracy in description of the linear and, in particular, nonlinear optical properties is strongly dependent on the level of accounting for the electron correlation effects. Thus, as is the case in *ab initio* methods, the form of the wave function used has to be capable of providing a very good representation of these effects. In our semiempirical calculations we have used a π-electron variant of the CC theory based on the Pople−Pariser−Parr (PPP)[8] model. It should be mentioned that in the past decade the PPP model has become increasingly more popular in predicting electrical and optical properties of large π-systems (for instance, refs 9 and 10 and references therein). Especially the nonlinear

molecular optical properties (hyperpolarizability) of long quasi-one-dimensional systems can be investigated fairly accurately with this model at relatively modest computational cost.[11−13] Despite the simplicity of the PPP Hamiltonian, our previous investigations[13−16] showed that the PPP-CC theory with single and double excitations (CCSD) can provide rather accurate (hyper)polarizability values. The direct comparison with the *ab initio* results, with the available experimental data, and with the results obtained using the π-electron approximation within the full configuration interaction (FCI) model[17,18] demonstrated reasonably good accuracy of the π-electron PPP-CCSD approach.[15,16]

However, the standard CCSD theory, even in combination with the simple PPP model, is still computationally demanding when applied to large (and long) π-polymeric systems. A possible way to further reduce the computational cost in the PPP-CC model is to use the so-called "local approximation". In this approximation the CC reference determinant is built using localized molecular orbitals (LMO). The use of LMOs enables reduction of the computational effort by determining the range at which the electron interaction effects become insignificant and neglecting all the interactions outside this range in the calculation. Implementation of the local approach in the *ab initio* CCSD scheme (see refs 19 and 20 for details) has also enabled investigation of larger molecular systems.

A distinctive feature of the local CCSD approach we use is building the reference determinant with MOs of covalently unbonded molecules of ethylene (cue). It allows us to simplify the most expensive parts of calculations, which are the transformation of the two-electron integrals and the calculation of the nonlinear parts of the CC diagrams.[16] The cue representation is in line with the classical organic-chemistry representation of π-conjugated carbon-based molecules as a set of covalently bonded ethylene fragments. We term our local PPP-CC approach the cue-CCSD method. A number of test calculations performed for small molecules, as well as for some alternating polymeric systems,[15,16] showed that the cue-CCSD results are close to those obtained with other PPP-CC methods and with the PPP-FCI method.

To obtain polarizabilities and hyperpolarizabilities within the cue-CCSD scheme we use the finite field method (FF). There are two approaches which can be used within the FF single-reference semiempirical CCSD scheme. In the first one for every electric-field strength a separate HF calculation followed by a CCSD calculation is performed. We term this variant of the CCSD method the relaxed-CCSD (r-CCSD for short) method. The second variant is to perform the HF calculation only once at the zero field strength and then use the orbitals generated there in the CCSD calculations for other field strengths. This approach is termed the unrelaxed-CCSD (u-CCSD for short) method. In all cue-CCSD calculations performed in this work the unrelaxed FF approach is used. Our previous (hyper)polarizability calculations showed that the u-CCSD values obtained for quasi-one-dimensional systems are usually much closer to the FCI values than the values obtained with the r-CCSD approach.[13,16]

In the present work the cue-CCSD approach is employed in the polarizability and hyperpolarizability calculations of a series of π-conjugated nonalternant systems. Such systems, when there is no center of inversion, can have sizable first and second hyperpolarizabilities. The push−pull carbon-based π-conjugated systems, which belong to this group, are prospective suitable compounds for fabrication of new nonlinear optical materials. The nonalternating hydrocarbons, which are investigated in the present work, can be viewed as particular models of the push−pull systems. Also the fulvalene-like systems investigated here (we investigate only pure carbon systems of this kind) are push−pull systems. They are considered as prospective electrically conducting materials.

In the present work we compare the cue-CCSD results with the HF, second-order Møller−Plesset theory (MP2), r-CCSD, u-CCSD, and FCI results. In cases where the local cue-CCSD approach shows significant discrepancy with the FCI results we also use the relaxed CC method with the connected triple excitations (r-CCSDT), as well as of connected quadruple excitations (r-CCSDTQ), to obtain more precise results.

2. THE LOCAL π-ELECTRON COUPLED CLUSTER THEORY

The wave function in the standard CCSD[6,7,21] method is represented by following expression:

$$|\Psi_{CCSD}\rangle = e^{\hat{T}_1 + \hat{T}_2}|0\rangle \tag{1}$$

or in an expanded form as

$$|\Psi_{CCSD}\rangle = \left(1 + \hat{T}_1 + \left(\frac{1}{2}\hat{T}_1^2 + \hat{T}_2\right) + \left(\frac{1}{3!}\hat{T}_1^3 + \hat{T}_1\hat{T}_2\right) + \left(\frac{1}{4!}\hat{T}_1^4 + \frac{1}{2}\hat{T}_2^2 + \frac{1}{2}\hat{T}_1^2\hat{T}_2\right)...\right)|0\rangle \tag{2}$$

where $|0\rangle$ is the reference determinant (usually HF). The $\hat{T}_1$ and $\hat{T}_2$ are cluster operators that generate superposition of singly and doubly excited configurations from the reference determinant:

$$\hat{T}_1|0\rangle = \sum_{i,a} t_i^a |_i^a\rangle \tag{3}$$

$$\hat{T}_2|0\rangle = \sum_{(i,a),(j,b)} t_{ij}^{ab}|_{ij}^{ab}\rangle \tag{4}$$

Indices i, j and a, b enumerate the occupied orbitals and the virtual orbitals, respectively. The CC theory can also be reformulated in the terms of unitary group generators E_{ai} and E_{bj}:[22,23]

$$\hat{T}_1 = \sum_{i,a} t_i^a E_{ai} \tag{5}$$

$$\hat{T}_2 = \frac{1}{2} \sum_{(i,a),(j,b)} t_{ij}^{ab} E_{ai} E_{bj} \tag{6}$$

To obtain the CC equations for the CC amplitudes, the Schrödinger equation is projected onto all singly and doubly excited configurations:

$$\langle 0 E_{ia}|H - E_{CCSD}|\Psi_{CCSD}\rangle = 0 \tag{7}$$

$$\langle 0(2E_{ia}E_{jb} + E_{ja}E_{ib})|H - E_{CCSD}|\Psi_{CCSD}\rangle = 0 \tag{8}$$

where H is the electronic Hamiltonian and E_{CCSD} is the CCSD energy of the system. As usual, to obtain E_{CCSD} one projects the Schrödinger equation onto the reference determinant, $|0\rangle$:

$$\langle 0|H - E_{CCSD}|\Psi_{CCSD}\rangle = 0 \tag{9}$$

In the π-electron CCSD theory (methods cue-CCSD, r-CCSD, and u-CCSD) H is the PPP model Hamiltonian.[8] The

parametrization of H is constructed assuming that each carbon atom in the π-conjugated molecule contributes an electron and a $2p_z$ orbital to the π-electron system. The following standard PPP parametrization is used: the one-center Coulomb integrals are equal to $\Gamma_0 = \langle \mu\mu|\mu\mu \rangle = 11.13$ eV and the two-center integrals ($\Gamma_{\mu\nu} = \langle \mu\nu|\mu\nu \rangle$) are estimated according to the Ohno formula.[24]

"Idealized" geometries of the molecules are used in the calculations: all C−C bond lengths are 1.4 Å, all cycles (rings) are regular polygons, and all angles in noncyclic fragments are equal to 120°. The resonance integral for a pair of connected carbon atoms is equal to $t_0 = -2.274$ eV. In the alternating-bond variant of the calculations (for polyenes) the two alternated-bond resonance integrals are equal to

$$t_{\pm} = t_0(1 \pm t) \tag{10}$$

where the empirical parameter $t \approx 0.1$. The t-dependent parameter allows one to more correctly describe the lowest electron transitions in short polyenes.[25] The "+" and "−" signs correspond to the hopping integrals for the double and single bonds, respectively.

Despite the significant simplification of the CCSD theory within the π-electron framework, the calculation scheme is still a time-consuming task for long conjugated systems. Especially long are the calculations of the nonlinear optical parameters. A way out of this problem is to use the "local electron correlation" approach.[26,27] As mentioned, the main idea of this approach is the use of localized MOs (LMO) as one-electron basis functions in the calculation. This significantly simplifies the computational scheme particularly the two-electron transformation and the calculation of the nonlinear components of the CC amplitude equations. In the LMO approach it is straightforward to determine the range (also called the correlation radius, CR) beyond which the correlation between two electrons becomes insignificant. Accounting for the interelectron interaction beyond the CR is unnecessary because of its insignificant contribution to the total energy. Neglecting these interactions dramatically reduces the computational cost of the calculation.[28]

Several local approximations have been proposed in the CCSD framework. The ground-state local CCSD approaches were developed in refs 29. and 30. A local EOMCCSD theory was also implemented in refs 31 and 32.

Recently we proposed a new variant of the π-electron local theory which employs molecular orbitals of ethylene molecules as structural elements of the conjugated system. The approach is based on the classical representation of a conjugated molecule as a system consisting of connected ethylene molecules. Hence the wave function of the molecule in the zeroth-order approximation is a determinant (the reference determinant in the CCSD approach) which is constructed using the bonding MOs of the ethylene molecules (cue). The CCSD wave function with such a reference (cue-CCSD approach) involves excitations within and between the ethylene fragments. The test calculations performed with the cue-CCSD approach, as well as with other CC approaches, for some small π-conjugated systems[15,16] demonstrated a good agreement of the cue-CCSD results with the results of the FCI method. Also in ref 14 the influence of the choice of the positions of the double bonds in the molecule on the calculated electric properties was investigated, and it was shown that even the hyperpolarizabilities, which are usually the most sensitive to this choice, are not significantly affected by this choice.

To further investigate this point let us consider the naphthalene molecule. There are two ways of the double-bond arrangement in this molecule corresponding to the bond in the middle of the molecule being either a single bond or a double bond. For these two arrangements the values of the second hyperpolarizability obtained in the cue-CCSD calculations are 1.72×10^4 and 1.73×10^4, respectively. The values are very close to each other, thus showing the insensitivity of the second hyperpolarizability to choice of the double-bond arrangement used in the calculation. The two values are also rather close to the FCI result, which is 1.81×10^4 au.

3. MOLECULAR (HYPER)POLARIZABILITY CALCULATION

The energy of the system in homogeneous electric field **F** can be expanded[1,33] as

$$E(\vec{\mathbf{F}}) = E(0) - \mu_r F_r - \frac{1}{2}\alpha_{rs}F_r F_s - \frac{1}{3!}\beta_{rst}F_r F_s F_t$$
$$- \frac{1}{4!}\gamma_{rstu}F_r F_s F_t F_u - \dots \tag{11}$$

where indices r, s, t, u, ... correspond to the Cartesian coordinates $\{r,s,t,u\} = \{x,y,z\}$ (the Einstein summation convention is assumed). μ_r, α_{rs}, β_{rst}, and γ_{rstu} are the Cartesian components of the dipole moment, the polarizability, and the first and second hyperpolarizabilities, respectively. These quantities are obtained by the differentiation of eq 11 at the zero field:

$$\mu_r = \left.\frac{\partial E(\mathbf{F})}{\partial F_r}\right|_{\mathbf{F}=0}$$

$$\alpha_{rs} = \left.\frac{\partial^2 E(\mathbf{F})}{\partial F_r \partial F_s}\right|_{\mathbf{F}=0}$$

$$\beta_{rst} = \left.\frac{\partial^3 E(\mathbf{F})}{\partial F_r \partial F_s \partial F_t}\right|_{\mathbf{F}=0}$$

$$\gamma_{rstu} = \left.\frac{\partial^4 E(\mathbf{F})}{\partial F_r \partial F_s \partial F_t \partial F_u}\right|_{\mathbf{F}=0} \tag{12}$$

These derivatives can be calculated numerically using the FF approach. The FF method involves calculating the energy of the molecular system in weak electric fields. For example, to calculate the fourth-order derivative ($E^{(IV)}$) the following "five point" formula can be used:

$$\gamma \sim E^{(IV)} \approx \frac{(-E_{-2} + 4E_{-1} - 6E_0 + 4E_1 - E_2)}{\xi^4} \tag{13}$$

where ξ is the differentiation step and $E_{\pm m}$ are the energies of the system in the field with strengths $\pm m\xi$. To calculate the energy for a nonzero field the interaction of the system with the field needs to be added to the unperturbed Hamiltonian, H_0:

$$\hat{H}(\pm m\xi) = \hat{H}_0 \pm m\xi\hat{R} \tag{14}$$

where $\hat{R}$ is the dipole-moment operator. In an atomic orbital basis when the zero differential overlap approximation is assumed R is a diagonal matrix.

As it is well-known,[1,3] the dipole moment and the (hyper)polarizabilities can be represented by the corresponding invariants. For a planar π-conjugated system placed in the xy
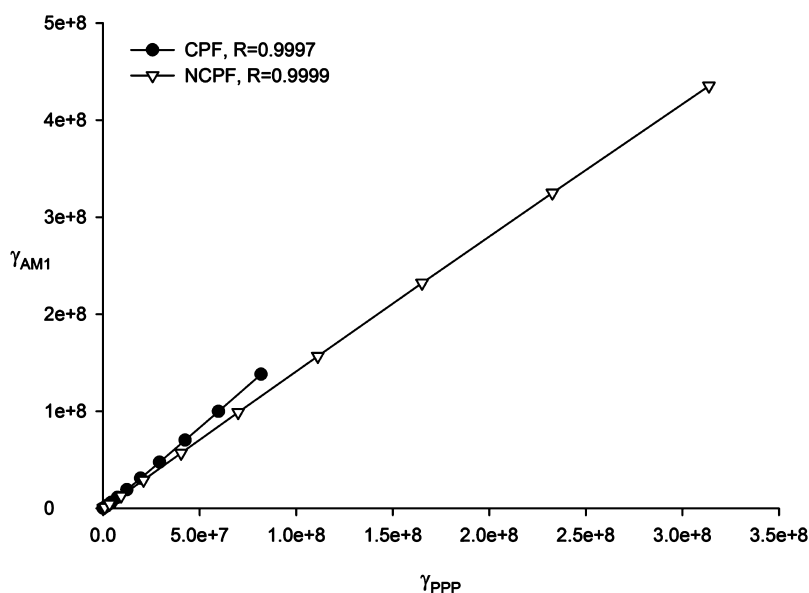
Figure 1. AM1 vs PPP-HF average hyperpolarizabilities for condensed (CPF, designated as circle) and noncondensed (NCPF, triangle) polyfulvenes (see Figure 7).

plane these invariants are represented by the following expressions:

$$|\mu| = \sqrt{\mu_x^2 + \mu_y^2}$$

$$\langle \alpha \rangle = \frac{1}{3}(\alpha_{xx} + \alpha_{yy})$$

$$|\beta| = \sqrt{(\beta_{xxx} + \beta_{xyy})^2 + (\beta_{yyy} + \beta_{yxx})^2}$$

$$\langle \gamma \rangle = \frac{1}{5}(\gamma_{xxxx} + \gamma_{yyyy} + 2\gamma_{xxyy}) \tag{15}$$

Since nonalternant hydrocarbons are systems with uneven charge distributions, their calculated electron densities provide information about the degree these distributions are asymmetric. The calculation of the one-electron reduced density matrix (RDM1) in the CC method is a nontrivial task. Several approaches have been developed for this purpose. Among them there is the so-called direct method based on the following equation:[21,34]

$$\rho_{rs} = \langle 0|e^{T^+}|s\rangle\langle r|e^T|0\rangle_C \tag{16}$$

where indices r and s correspond to spin−orbitals. Equation 16 can be implemented by truncating the expansions of the two exponentials in eq 1 at the components of a certain order (say, third- or fourth-order).

Another approach to calculate CC RDM1 is based on the CC response theory.[21] Here the matrix elements of RDM1 have the following form:

$$\rho_{rs} = \langle 0|(1 + \Lambda)|s\rangle\langle r|e^T|0\rangle_C \tag{17}$$

where Λ is a de-excitation operator which is obtained by solving the corresponding linear "Λ-equation". For a detailed description of the method see ref 21. A spin-adapted LR approach to calculate the RDM was described in ref 35.

Approaches 16 and 17 involve calculations of a significant number of CC diagrams and can be computationally demanding especially for larger systems. However, in the

framework of the π-electron approximation it is quite simple to obtain atomic densities as the diagonal matrix elements of the RDM1 matrix. The off-diagonal matrix elements are the π-electron bond orders. These elements are derivatives of the energy with respect to the matrix elements of the core Hamiltonian, h_{rs}:

$$\rho_{rs} = \frac{1}{2 - \delta_{rs}}\frac{\partial E}{\partial h_{rs}} \tag{18}$$

where δ_{rs} is the Kronecker delta. According to our experience the derivative 18 can be determined with a satisfactory accuracy using the simple numerical-derivative "two-points" formula:

$$\rho_{rs} \approx \frac{E(h_{rs} + \xi) - E(h_{rs} - \xi)}{2\xi} \tag{19}$$

where ξ is a sufficiently small step.

The calculations of the perturbed energies, $E(h_{rs} \pm \xi)$, can be performed with either the relaxed or the unrelaxed model. In the first case the matrix elements of the core Hamiltonian are altered before the calculation of the orbitals (r-CCSD method) while in the second case the matrix elements are altered after the calculation of the orbitals (u-CCSD method). The approaches based on eqs 16−18 are implemented in our computer code. The simplest way to calculate RDM1 based on eqs 18 and 19 provides results which are close to the FCI results, as well as to those obtained with the approaches based on eqs 16 and 17.

4. NUMERICAL ILLUSTRATION

In the present calculations of the optical properties the following polymer systems are considered: *trans*-polyene [PE], poly *p*-quinodimethane [PQ], polyphenylene vinylene [PPV], condensed polyfulvenes [CPF], and noncondensed polyfulvenes [NCPF]). The bond-alternation model (eq 10) is employed in the calculations. In the calculations of poly calicene (PC) and of the monomers of all considered systems the parametrization which does not take into account the bond

alternation is used. Figures depicting these schemes are shown below.

An important question which can be raised is how the (hyper)polarizability results obtained with the PPP methods compare with the results of other methods, particularly with the *ab initio* methods, and how close they are to the results obtained in the experiment. Some comparison of this kind was already presented in our previous works. For example, the hyperpolarizabilities of *trans*-polyenes were compared with the experimental values in ref 13, and it was demonstrated that the π-electron CCSD approach gives rather close values for the hyperpolarizabilities to experimental ones.

Let us now compare the results of the π-electron calculations with the results obtained from other quantum chemical approaches. The first comparison concerns the average hyperpolarizability $\langle \gamma \rangle$ (eq 15) obtained at the Hartree−Fock level of theory in π-electron approximation (PPP) and obtained with all-valence AM1 approach. The comparison is shown in Figure 1. The calculations are performed for condensed (CPF) and noncondensed (NCPF) polyfulvenes (see Figure 8) with the number of the periodic units up to $N = 14$. GAMESS package[36] is used in the AM1 calculations. As one can see, the PPP HF results agree very well with the AM1 results. The corresponding correlation coefficients, R, are close to unity. This shows that the most important contribution to the second hyperpolarizability arises from the electrons in the π-shell of the molecule while the contribution from the σ-shell electrons is smaller and constant.

The next example concerns a comparison of the PPP with the results obtained from *ab initio* calculations performed at the MP2/6-31++G(d,p) level of theory. The comparison of the calculations performed for the elementary units of the CPF and NCPF systems is presented in Table 1. As one can see, the

Table 1. Comparison of $\langle \gamma \rangle$ Obtained in π-Electron MP2 Calculation with the PPP Hamiltonian and in *ab Initio* MP2/6-31++G(d,p) Calculations

Unit	π-electron MP2	MP2 /6-31++G(d,p)
CPF	$0.5 \cdot 10^5$	$0.37 \cdot 10^5$
NCPF	$1.71 \cdot 10^5$	$0.64 \cdot 10^5$

values of $\langle \gamma \rangle$ obtained at the MP2 level with the semiempirical and nonempirical approaches are reasonably close to each other. This provides validation of the use of the π-electron approximation in the (hyper)polarizability calculations performed in the present work.
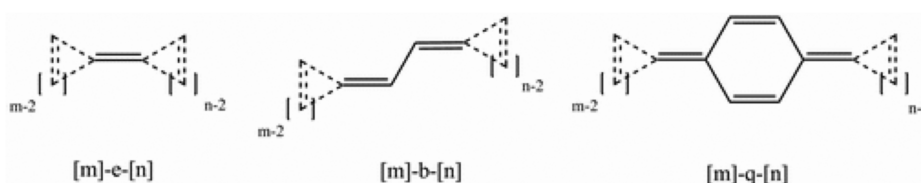
4.1. Fulvalenes and Fulvalene-like Systems. The first systems calculated here are fulvalenes and fulvalene-like molecules. For simplicity we encrypt all considered fulvalene-like systems as derivatives of ethylene (e), *trans*-butadiene (b), or *p*-quinodimethane (q) (as shown in Figure 2).

These systems are chosen for testing of the approach because they all have significant π-electron dipole moments. Despite the fact that these molecules are built only of carbon, they all show a notable intramolecular charge transfer.[37] Our interest in these systems is related to the recent synthesis of the three- and four-member oligomers of calicene.[38,39] The theoretical investigations[40,41] demonstrated the aromatic nature of the systems which results from the tendency of their cycles to form aromatic $(4n + 2)$ perimeters. For example, let us examine this phenomenon for the calicene molecule. According to the convention of Figure 2 calicene can be designated as a [3]-e-[5] molecule (three- and five-member rings joined by a double bond; Figure 3).
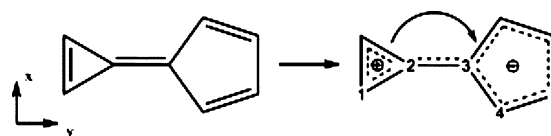

Figure 3. The direction of charge transfer in the calicene molecule.

The π-charges calculated using different methods for the calicene molecule are presented in Table 2. Relative to the FCI results, a less complete accounting for the electron correlation causes a decrease of the charges located on the cycles.

Table 2. Charges on Atoms in [3]-e-[5] Obtained with Different Approaches[a]

	atom					
	1	2	3	4	5	δ
Hückel	0.281	0.262	−0.181	−0.157	−0.165	0.824
HF	0.145	0.156	−0.150	−0.088	−0.060	0.445
MP2	0.141	0.131	−0.126	−0.089	−0.054	0.412
cue-CCSD	0.129	0.088	−0.085	−0.090	−0.040	0.346
u-CCSD	0.125	0.085	−0.091	−0.082	−0.039	0.334
r-CCSD	0.125	0.087	−0.094	−0.081	−0.040	0.336
FCI	0.124	0.081	−0.089	−0.085	−0.039	0.330

[a]δ is the charge transferred between the two cycles (all values are in electron units).

As it can be seen from Table 2, the accuracy in accounting for the electron correlation strongly affects the value of the calculated transferred charge (δ). The simplest π-electron Hückel method overestimates δ more than twice. Despite the MP2 approach being able to account for a significant part of the electron correlation effects, it does not give better results than

Figure 2. Fulvalenes and fulvalene-like systems and the corresponding symbolic designations of them used in this work.

the HF method. The error is still around 25% relative to the FCI results. At the same time, all CC methods give good agreement with the FCI results. Even the cue-CCSD results show an error smaller than 5%. Thus, as the computational demands of the FCI method do not allow calculations of the electron density for large molecules, we use the densities obtained in the cue-CCSD calculations as the reference results in the rest of this work.

The significant dependence of the intramolecular charge transfer on the level of accounting for the electron correlation suggests that, perhaps, a reliable description of a system's electric properties may be difficult to achieve. Further calculations confirm this suspicion. In the calculations of the nonlinear optical parameters we find that even for such a small system as [3]-e-[5] both r-CCSD and u-CCSD methods show large errors (for the components of the second hyper-polarizability along the molecular axis) of about 30%. The CCSDT and CCSDTQ calculations show that connected higher-level excitations make an important contribution to the nonlinear optical parameters. The components of the polar-izability and the first and second hyperpolarizabilities obtained with the different approaches are presented in the Table 3.

Table 3. Components of the Polarizability and the First and Second Hyperpolarizabilities Calculated with Different Approaches (in au)[a]

[3]-e-[5]	α_{xx}	α_{yy}	β_{yyy}	$\gamma_{xxxx}/10^3$	$\gamma_{yyyy}/10^4$
HF	43.8 (9.3)	119.4 (−0.6)	−362 (−118.9)	8.05 (−15.8)	−4.74 (−20.9)
MP2	42.4 (5.7)	119.4 (−0.7)	159 (−91.7)	8.85 (−7.4)	−5.91 (−1.5)
cue-CCSD	40.2 (0.3)	123.8 (3.0)	1868 (−2.5)	9.37 (−2.0)	−8.23 (−37.1)
u-CCSD	40.5 (1.0)	122.9 (2.3)	1752 (−8.6)	9.11 (−4.7)	−9.07 (−51.2)
r-CCSD	40.3 (0.5)	121.8 (1.4)	1726 (−9.9)	9.07 (−5.1)	−7.85 (30.8)
r-CCSDT	40.2 (0.2)	120.5 (0.2)	1902 (−0.7)	9.37 (−2.0)	−6.31 (5.2)
r-CCSDTQ	40.1 (0.0)	120.2 (0.0)	1916 (0.0)	9.48 (−0.8)	−6.03 (0.5)
FCI	40.1	120.2	1916	9.56	−6.00

[a]The error relative to FCI is shown in parentheses (in %).

Despite the fact that the CCSD method accounts, on average, for almost 97% of the correlation energy, it is still not enough for an adequate description of the first and second hyper-polarizabilities by this method. Inclusion of the connected triple excitations (using r-CCSDT) reduces the error in γ to about

5%, while inclusion of the quadruple excitations (in r-CCSDTQ) produces results virtually identical to the FCI result. It should also be noted that the very good MP2 value of γ_{yyyy} is likely a coincidence, as this method gives wrong results for the other fulvalene-like systems (see Table 5). The results for the first and second hyperpolarizabilities are presented in Tables 4 and 5 (the tables only include systems where the FCI results are available).

The results demonstrate that all mentioned molecules can be separated into three classes. The systems where charge transfer does not occur for the symmetry reason ([m] = [n]) belong to the *first class*. For this class the CC methods show relatively small error in the calculation of the second hyperpolarizability. This small error suggests that the difficulty in getting reliable hyperpolarizabilities in the CC calculations is related not to the nonalternating nature of the bonding structure in these systems but to an inadequate description of the intramolecular charge transfer by the CC method without triples and quadruples. The *second class* (Figures 3 and 4) comprises molecules where π-electron delocalization may result in the formation of two aromatic rings ($4n + 2$ rule). The *third class* comprises systems with two rings, one aromatic and one antiaromatic (Figure 5). The CC calculations show that for the second class systems there is a minor error in the $|\beta|$ values and a large error for $\langle \gamma \rangle$. For the systems in the third class the opposite happens.

In the third-class systems there is small charge transfer from the smaller to the larger ring. For instance, while the charge transfers are $\delta_{[3]-e-[5]} = 0.346$ and $\delta_{[3]-e-[9]} = 0.304$, the charge transfer for the [3]-e-[7] is only 0.128. Whether the charge transfer is small or large is related to the competing tendencies of the two rings to attract electrons. A small value of δ reflects opposite tendencies of small and large cycles to form aromatic π-electron bonding systems. This is why the level of accounting for the electron correlation is key in correctly describing the electric properties in the calculations, especially the first hyperpolarizability which directly depends on the charge distribution. As the second hyperpolarizability ($\langle \gamma \rangle$) has no direct dependency on the charge distribution, all CC methods provide a quite good description of $\langle \gamma \rangle$ for the third-class systems.

As for the derivatives of *trans*-butadiene (and quinodi-methane), they reveal slightly different electron density distributions than the corresponding ethylene derivatives. The bridge between the rings (the binding fragment, **bf**) provides additional electrons and holes for the rings which either increase or decrease the ring charges (Table 6).
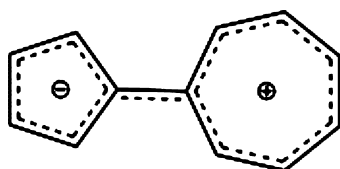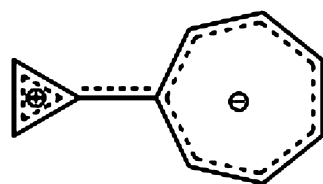
The charge transfer between the cycles and **bf** for the fulvalene-like systems is shown in Figure 6. In the first type of

Table 4. 1st Hyperpolarizability $|\beta|$ Calculated with Different Approaches (in au)

	class	HF	MP2	cue-CCSD	r-CCSD	u-CCSD	FCI
[3]-e-[5]	2	456	123	1926	1766	1792	1964
[3]-e-[7]	3	178	470	1317	938	941	1147
[3]-e-[9]	2	252	1687	6946	6711	6580	6734
[5]-e-[7]	2	1895	495	7200	7663	7714	8088
[5]-e-[9]	3	1850	673	1722	1502	1371	1939
[3]-b-[5]	2	980	2969	9758	9442	9137	9221
[3]-b-[7]	3	1425	1957	2898	2166	2192	2445
[3]-b-[9]	2	3279	7923	19278	21294	20084	19273
[5]-b-[7]	2	1365	6363	19655	22504	21163	20178
[3]-q-[5]	2	7541	6370	34199	46597	43400	40800

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Table 5. 2nd Hyperpolarizability $\langle\gamma\rangle/10^4$ Calculated in Different Approaches (in au)

	class	HF	MP2	cue-CCSD	r-CCSD	u-CCSD	FCI
[3]-e-[3]	1	0.29	0.40	0.79	0.92	0.88	1.03
[3]-e-[5]	2	−0.88	−1.09	−1.33	−1.24	−1.53	−0.84
[3]-e-[7]	3	0.02	1.52	5.61	5.29	5.21	5.53
[3]-e-[9]	2	−1.96	−1.60	8.44	5.88	4.83	8.32
[5]-e-[5]	1	−0.99	1.04	6.73	6.16	6.12	6.78
[5]-e-[7]	2	−4.69	−4.31	4.42	2.51	1.60	8.33
[5]-e-[9]	3	−1.60	5.35	22.68	21.75	20.95	22.21
[7]-e-[7]	1	−4.79	5.48	25.74	25.19	23.98	25.42
[3]-b-[3]	1	1.24	2.25	4.67	4.78	4.55	4.88
[3]-b-[5]	2	−2.45	−0.89	14.85	13.55	12.06	15.34
[3]-b-[7]	3	1.68	8.31	22.60	22.10	20.71	21.50
[3]-b-[9]	2	−4.77	2.69	57.13	62.24	53.94	63.53
[5]-b-[5]	1	2.63	9.85	25.26	24.34	23.20	24.06
[5]-b-[7]	3	−8.63	1.92	59.90	67.59	60.19	71.44
[3]-q-[3]	1	−4.56	8.61	30.51	34.96	30.74	31.07
[3]-q-[5]	2	−28.99	−31.44	37.42	91.76	90.59	135.29

Figure 4. Formation of two $6e^-$ (5- and 7-centered) aromatic rings for [5]-e-[7].

Figure 5. $2e^-$ and $8e^-$ rings of [3]-e-[7].

derivatives the charge transfer appears between the rings and **bf** and brings the π-electron ring structure to an aromatic state. However, this effect fades out swiftly with the growth of the rings and seems to approach zero in the limit. For the second class, **bf** prevents a direct conjugation of the cycles and thereby decreases the electron exchange between them as compared to

fulvalenes. Still this does not reduce the dipole moment and the first hyperpolarizability (see the $|\beta|$ values for [3]-e-[5], [3]-b-[5], and [3]-q-[5] in Table 4). In the case of p-quinodimethane the phenomena described above are mostly observed for the *trans*-butadiene systems (i.e., for the systems of classes 1 and 2: $\delta_{bf}(\text{quinodimethane}) > \delta_{bf}(\text{butadiene})$, while for the class 3 systems, $\delta_{bf}(\text{quinodimethane}) \sim \delta_{bf}(\text{butadiene})$).

4.2. Nonclassical "Push–Pull" Polymers. To design materials with desired nonlinear optical properties (especially with the appropriate $|\beta|$), one should choose systems belonging to the second class. In these systems the electron-transfer effects introduced by the left and right cycles (e.g., three- and five-member cycles) are similar to the effects of the end-groups in push–pull systems, which are known to possess significant optical nonlinearities. However, they differ from the latter as they are pure carbon systems and, thus, only the π-electrons are involved in the charge transfer. Of course, the type and the length of **bf** can be a significant factor in the electron charge distribution. As examples, the bridge systems PE, PQ, and their combination, and the PPV system are investigated (Figure 7).

The redistribution of the charges between the end-rings in the polymer and **bf**, and the π-contribution puts limits on the size of the dipole moment, $|\mu|$, of the polymer (despite the continued growth of the **bf** length). An estimation of the limit
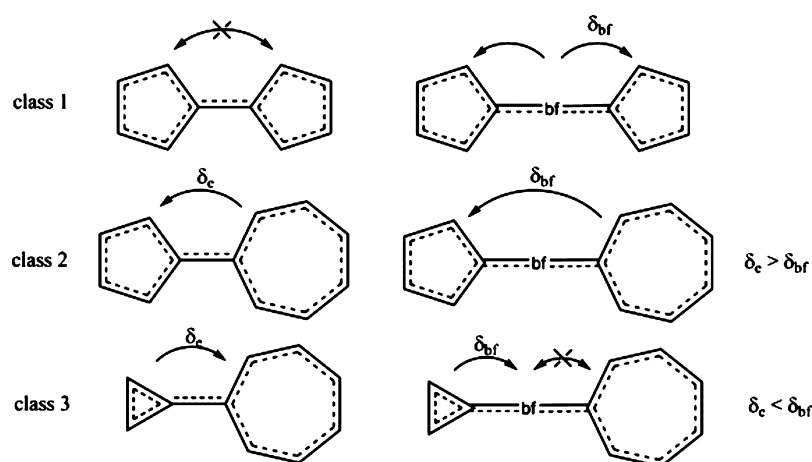

Figure 6. Three classes of fulvalenes and fulvalene-like systems (see Table 6).

Table 6. cue-CCSD Charges on the Two Cycles Calculated as $\sum q_{\{1\}}$ and $\sum q_{\{2\}}$ for the Studied Systems[a]

[1st]-**bf**-[2nd]	class	double bond		trans-butadiene			p-quinodimethane		
		$\sum q_{\{1\}}$	$\sum q_{\{2\}}$	$\sum q_{\{1\}}$	$\sum q_{\{bf\}}$	$\sum q_{\{2\}}$	$\sum q_{\{1\}}$	$\sum q_{\{bf\}}$	$\sum q_{\{2\}}$
[3]-bf-[3]	1	0.000	0.000	0.118	−0.236	0.118	0.125	−0.250	0.125
[5]-bf -[5]		0.000	0.000	−0.069	0.138	−0.069	−0.074	0.148	−0.074
[7]-bf -[7]		0.000	0.000	0.049	−0.098	0.049	0.054	−0.108	0.054
[3]-bf -[5]	2	0.346	−0.346	0.262	−0.040	−0.222	0.277	−0.039	−0.238
[3]-bf -[9]		0.304	−0.304	0.246	−0.069	−0.177	0.257	−0.065	−0.192
[5]-bf -[7]		−0.253	0.253	−0.184	0.017	0.167	−0.192	0.015	0.177
[7]-bf -[9]		0.196	−0.196	0.142	−0.013	−0.129	0.151	−0.012	−0.139
[3]-bf -[7]	3	0.128	−0.128	0.169	−0.163	−0.006	0.170	−0.174	0.004
[5]-bf -[9]		−0.077	0.077	−0.105	0.103	0.002	−0.105	0.112	−0.007

[a]Residual charge of the bridge is calculated as $\sum q_{\{bf\}}$. All charges are in the units of electron.
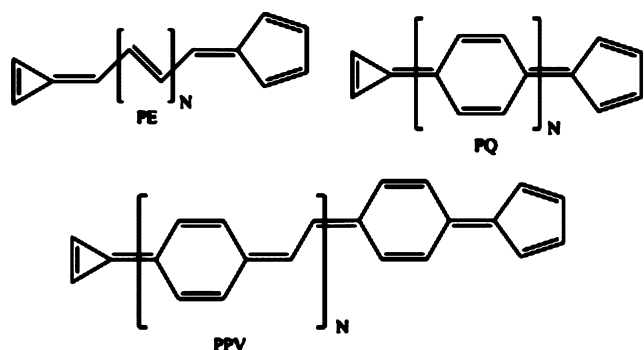

Figure 7. [3]-bf-[5] polymers considered in the present study.

values of the π-electron dipole moment, when the number of elementary units (N) and/or the number of π-electrons (N_{el}) grows, shows that $|\mu|$ converges rather fast. The limit values are different for the different bridges (see Table 7).

Table 7. π-Electrical Parameters for [3]-bf-[5] Systems Obtained from cue-CCSD Method

bridge	$|\mu|$ (D)	$\langle\alpha\rangle^{\infty}/N_{el}$ (au)	$|\beta|^{\infty}$ (au)	$\langle\gamma\rangle^{\infty}/N_{el}$ (au)
PE	5	14	2×10^4	2×10^5
PQ	14	>55[a]	1×10^6	>2×10^{7a}
PPV	9	29	2×10^5	2×10^6

[a]Extrapolation of dependence is not reliable because of intensive growth.

Based on the above, one can reason that the first hyperpolarizability ($|\beta|^{\infty}$) also converges to a constant value when the oligomer length increases. Indeed, as the results show, this value converges fast with the system length.

The average polarizability value calculated per-electron ($\langle\alpha\rangle^{\infty}/N_{el}$) and the analogical value of the second hyperpolarizability ($\langle\gamma\rangle^{\infty}/N_{el}$) should behave in the same way. The polarizability and hyperpolarizability per π-electron for an infinite chain are estimated by extrapolating of the corresponding α and γ values to infinite N. To evaluate $\langle\alpha\rangle^{\infty}/N_{el}$ and $\langle\gamma\rangle^{\infty}/N_{el}$ we use the dependence of the corresponding average values on the inverted number of π-electrons ($1/N_{el}$). For large N we assume linear behavior of $\langle\alpha\rangle/N_{el}$ and $\langle\gamma\rangle/N_{el}$ with $1/N_{el}$. The values for the linear region of the curve are obtained by the least-squares method using ten-point extrapolation. In all calculations the correlation coefficients, which correspond to the linear part of the curve, are never less than 0.999. For more

details concerning the extrapolation scheme see our previous article.[16]

It should be noted that using the extrapolation fast convergence is only obtained for the systems with the PE and PPV bridges. For the systems with **bf** = PQ a fast increase of the average polarizability and the hyperpolarizability is observed when $N_{el} \rightarrow \infty$. Hence the corresponding limit values shown for these systems in Table 7 are only approximate.

The PQ systems have the most distinct set of electro-optical characteristics in comparison with the other considered polymers. A large value of the limit for the second hyperpolarizability $\langle\gamma\rangle^{\infty}/N_{el}$ is caused not only by the presence of the push−pull ending groups but also by **bf** itself. According to the present calculations the $\langle\gamma\rangle^{\infty}/N_{el}$ values for the poly p-quinodimethane (PQ) chains are not smaller than 10^7 au.

4.3. Polyfulvenes and Polycalicenes. Three more types of polymeric systems are considered in this work (Figure 8): condensed polyfulvenes (CPF), noncondensed polyfulvenes (NCPF), and polycalicene (PC). These macromolecules can be identified by where a perturbation is introduced to the alternating monomeric units.
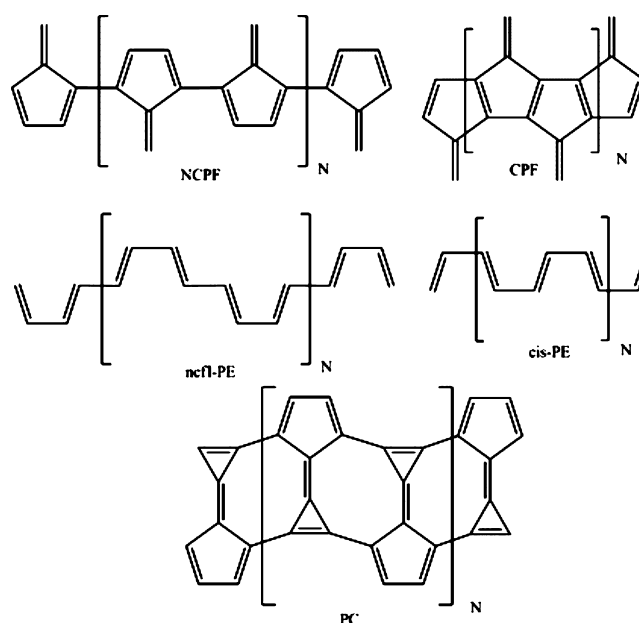

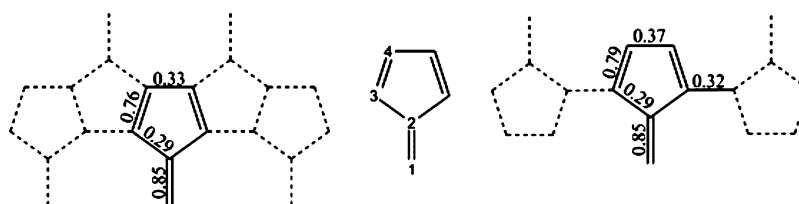**Figure 8.** The investigated polymeric systems.

Figure 9. cue-CCSD bond orders.

CPF and NCPF may be regarded as polyene derivatives with the ethylene groups being the perturbing units (noncondensed fulvene-like PE (ncfl-PE) and cis-PE, respectively). PE[16] exhibits significant optical nonlinearity. The perturbing units are likely to greatly affect the electron-optical properties of the systems. As the probe to characterize the effect of the ethylene groups on the polyene chains we use the cue-CCSD bond orders expressed by the off-diagonal RDM1 matrix elements (Figure 9).

By comparing these values and the other elements of RDM (Table 8) for the different elementary units of the quasi-infinite

Table 8. Atomic Charges for Monomer Units in the Quasi-Infinite Chains in Comparison with the Corresponding Values for Fulvene (Atom Numbering According to Figure 9)

	atom			
	1	2	3	4
CPF	0.040	0.031	−0.035	−0.035
NCPF	0.070	0.018	−0.026	−0.018
pentafulvene	0.099	0.030	−0.064	≈0.000

chains (where the electron densities are close to the limit values) one observes similarities in the electron distributions in the CPF and NCPF oligomers.

The impact of the structural perturbation can be also illustrated by the second hyperpolarizability values. As can be seen from Figure 10, the CPF and NCPF systems show significant decreases of $\langle\gamma\rangle$ in comparison with the corresponding polyene even for short oligomers.

It should be noted that there is no significant difference in $\langle\gamma\rangle$ for the geometrically different polyenes (cis-PE and ncfl-PE). Also, there is no significant difference for the polyfulvenes (CPF and NCPF). A similar situation is observed for the polarizability. Most clearly it can be seen by examining the limit values of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ shown in Table 9.

Table 9. Calculated Limits of the Specific Average Polarizability and 2nd Hyperpolarizability (in au)

	cis-PE	CPF	ncfl-PE	NCPF
$\langle\alpha\rangle^\infty/N_{el}$	9.5	7.0	9.7	6.6
$\langle\gamma\rangle^\infty/N_{el}$	9.8×10^4	5.8×10^4	9.9×10^4	5.2×10^4

Analyzing the charge distribution for an isolated monomer unit and the monomer unit in a quasi-infinite polymer one notices that the existence of the conjugated chain lowers the charge transfer relative to the isolated fulvene. Therefore it cannot be expected that CPF and NCPF have large first hyperpolarizabilities. The estimated values of $|\beta|^\infty$ for CPF and NCPF (for odd units in the chain) are equal to 29 au and 310 au, respectively. The latter value can be compared with the corresponding value for the monomeric fulvene of 510 au.

The failure of the additive scheme to estimate the second hyperpolarizability (as well as the polarizability) for long oligomers can be illustrated on polyfulvenes. As the periodic unit (pu) for these systems we use the butadiene for the CPF and fulvene for NCPF (Figure 11).

The limit, specific (per pu) values obtained in the calculations of $\langle\gamma\rangle$ for the oligomer chains compared with the
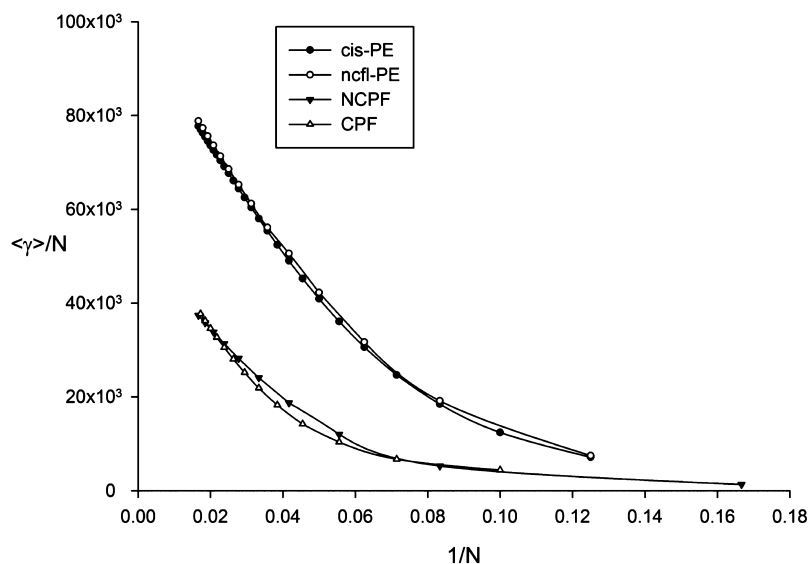

Figure 10. Specific 2nd hyperpolarizability vs inverse of the number of π-electrons.

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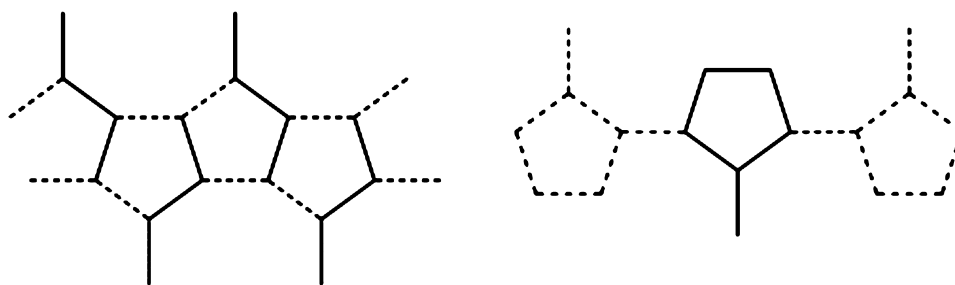dx.doi.org/10.1021/jp5002176 | J. Phys. Chem. C 2014, 118, 8111−8121

Figure 11. Periodic units for CPF and NCPF.

corresponding values obtained for separate pu's are shown in Table 10.

Table 10. Comparison of the Specific Values (per pu) of $\langle\alpha\rangle$ and $\langle\gamma\rangle$ Obtained by Extrapolation[a]

	pu	extrapolation	relative error
CPF			
$\langle\alpha\rangle^{\infty}$/pu	17.1	28.0	−39%
$\langle\gamma\rangle^{\infty}$/pu	6.7×10^3	2.3×10^5	−97%
NCPF			
$\langle\alpha\rangle^{\infty}$/pu	26.7	39.6	−33%
$\langle\gamma\rangle^{\infty}$/pu	7.9×10^3	3.2×10^5	−98%

[a]All values are in au.

Obviously the additive scheme is unable to estimate correctly the (hyper)polarizabilities because this scheme is unable to reproduce the monomeric properties accurately. It is also interesting that for different monomeric units for systems which otherwise are structurally similar (systems which are expected to possess similar properties) one obtains close estimates.

The (hyper)polarizabilities for calicene (Figure 3) and polycalycene (PC, Figure 8) molecules are another example of the additive scheme not working well. The calculated values for the limit, unit-specific $\langle\alpha\rangle^{\infty}_{\text{extr}}$/pu = 163.4 au and $\langle\gamma\rangle^{\infty}_{\text{extr}}$/pu = 3.3×10^6 au for polycalicenes reveal the essentially nonadditive character of the linear and nonlinear optical properties of these systems (the relative errors for these quantities are over −67% and −99.5%, respectively).

5. CONCLUSION

Despite intense activity in the field of predicting linear and nonlinear optical properties of molecular systems, there is still a large amount of open problems that need to be solved. These include the need to developed new, improved quantum chemistry methods for calculating these properties. A large number of polymeric systems of significant practical interest are still beyond the computational capabilities of modern science. The existing calculations show that in the study of optical properties one needs to choose between either performing more exact calculations, but for smaller systems, or more approximate calculations for larger systems. The calculations carried out in the present work show a complete failure of methods without or with more approximate account of the electron correlation effects in predicting the optical properties of molecular systems (wrong signs and/or the order of magnitude). Even the use of such a flexible method as CCSD reveals a considerable error in the hyperpolarizability calculations even for smaller molecules. This error seems to originate from the inability of the CCSD method to correctly

describe the intramolecular charge transfer. This point requires further investigation.

Based on the present results we can unequivocally say that the local π-electron semiempirical variant of the CC theory can be successfully used in calculating optical properties of large and long strongly correlated π-systems. In general, the calculations demonstrate a large range of values of the electrical susceptibility in polymeric systems. It is likely that a polymer with the right susceptibility for the particular application can be found. For example, the "non-classic push−pull" polymeric systems (especially containing a p-poly quinodimethane bridge) have susceptibilities that make them potentially good materials for the fabrication of electron-optical devices.

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Notes

The authors declare no competing financial interest.

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