Linear and Nonlinear Optical Properties of [60]Fullerene Derivatives

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Using a wide variety of quantum-chemical methods we have analyzed in detail the linear and non-linear optical properties of [60]fullerene−chromophore dyads of different electron-donor character. The dyads are composed of [60]fullerene covalently linked with 2,1,3-benzothiadiazole and carbazole derivatives. Linear scaling calculations of molecular (hyper)polarizabilities were performed using wave function theory as well as density functional theory (DFT). Within the former approach, we used both semiempirical (PM3) and *ab initio* (Hartree−Fock and second-order Møller−Plesset perturbation theory) methods. Within the latter approach only the recently proposed long-range (LRC) schemes successfully avoid a large overshoot in the value obtained for the first hyperpolarizability (β). Calculations on model fullerene derivatives establish a connection between this overshoot and the electron-donating capability of the substituent. Substitution of 2,1,3-benzothiadiazole by the triphenylamine group significantly increases the electronic first and second hyperpolarizabilities as well as the two-photon absorption cross section. For [60]fullerene−chromophore dyads we have, additionally, observed that the double harmonic vibrational contribution to the static β is much larger than its electronic counterpart. The same is true for the dc−Pockels β as compared to the static electronic value, although the vibrational term is reduced in magnitude; for the intensity-dependent refractive index the vibrational and electronic terms are comparable. A nuclear relaxation treatment of vibrational anharmonicity for a model fulleropyrrolidine molecule yields a first-order contribution that is substantially more important than the double harmonic term for the static β.

1. Introduction

During recent years significant progress has been made in the synthesis and characterization of photoactive materials.[1] In particular, tremendous efforts have been invested in the design of materials exhibiting high nonlinear optical response. A plethora of organic[2,3] and organometallic[4,5] systems have been studied in this context.

One of the most common strategies for design of new molecules with high values of the first hyperpolarizability (β) has its roots in the so-called two-state model proposed in the late seventies.[6] Within this model, β is expressed in terms of (i) the dipole moment difference, (ii) the transition dipole moment, and (iii) the energy difference between the key charge transfer excited-state and the ground electronic state. Numerous molecular systems of diverse donor−acceptor (DA) character have been proposed according to the two-level model in order to maximize β.

[60]Fullerene is an especially interesting acceptor molecule. When combined with photo- and/or electro-active moieties an efficient charge separation and slow charge recombination occurs due to its small reorganization energy. Many [60]fullerene-based hybrid materials with porphyrins,[7] tetrathiafulvalenes[8] and ferrocenes[9] have been prepared and studied in the past. Recently, several dyad systems wherein [60]fullerene is combined with the carbazole, benzothiazole and benzothiazole−triphenylamine moieties have been synthesized[10,11] (**1**−**3** in Figure 1, respectively) with an eye toward their potential usefulness as photonic materials. The primary goal of the present contribution is to calculate and analyze the nonlinear optical properties of these dyad systems.

Each of the chromophores mentioned above is interesting in its own right. Carbazole is an organic compound which exhibits unusual photophysical properties, such as the photoconductivity observed in poly(vinylcarbazole).[12] On the other hand, 4,7-diphenyl-2,1,3-benzothiazole-based compounds are strongly fluorescent dyes,[13,14] which have absorption and emission profiles that can be easily tuned by substitution at the aryl unit of the benzothiazole moiety. Finally, triphenylamine (TPhA) based materials are widely known as excellent hole-transporters

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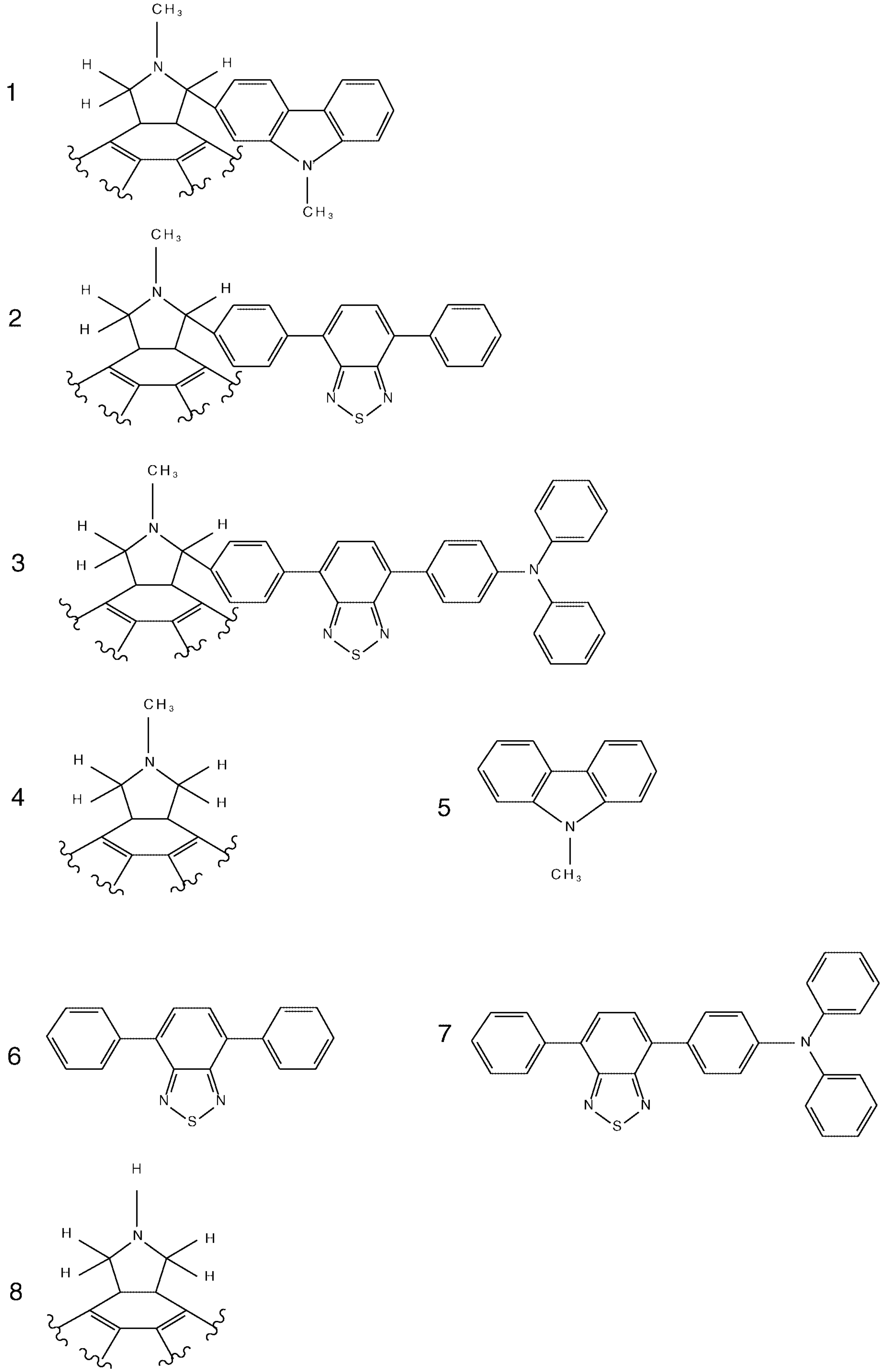


Figure 1. Schematic representation of investigated molecules.

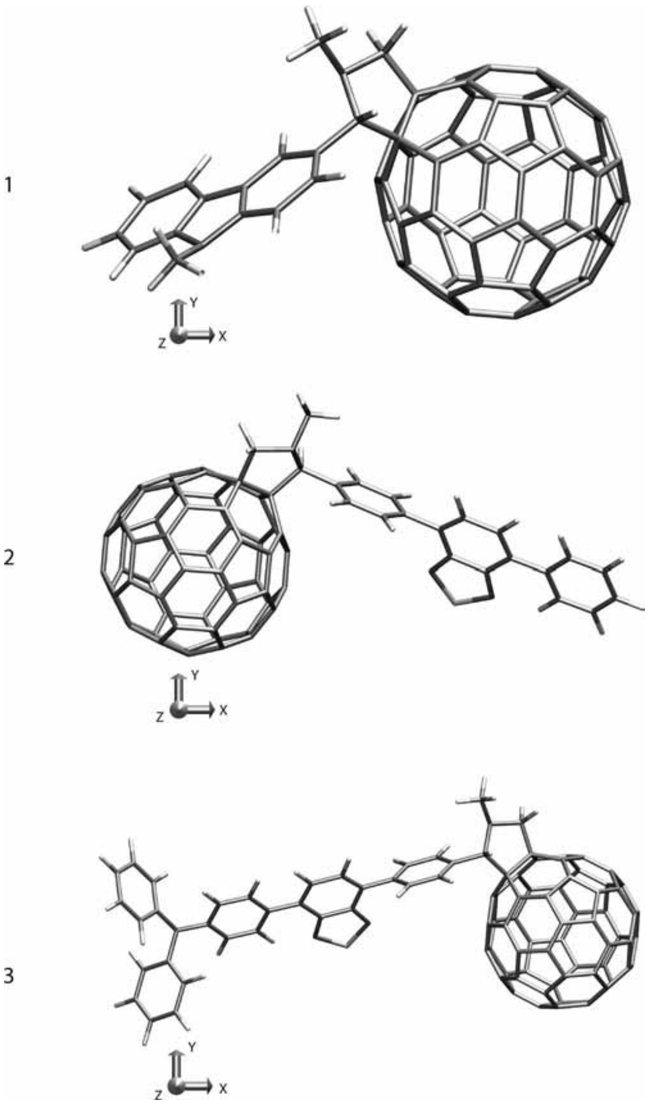


Figure 2. Structure of investigated [60]fullerene derivatives. Shown is the orientation of Cartesian directions used in property calculations.

TABLE 2: Dipole Moment μ and Average Polarizability $\bar{\alpha}$, First Hyperpolarizability $\bar{\beta}$, and Second Hyperpolarizability $\bar{\gamma}$ of 1 Calculated at the HF/6-31G(d) Level of Theory for the Structures Optimized Using PM3 and B3LYP/6-31G(d)[a]

	PM3 geometry	B3LYP/6-31G(d) geometry
μ	1.72	1.92
$\bar{\alpha}$	634.09	640.33
$\bar{\beta}$	403.33	470.14
$\bar{\gamma}$	71279	70414

[a] All values are given in atomic units.

TABLE 3: Calculated Diagonal *x*-Component for Electronic Dipole Moment μ_x, Linear Polarizability (α_{xx}) and First Hyperpolarizability (β_{xxx}) of 1[a]

method	μ_x	α_{xx}	β_{xxx}
HF/3-21G	−1.79	681.87	−661.1
HF/6-31G(d)	−1.47	735.27	−558.1
MP2/6-31G(d)	−1.67	782.99	−1301.2
MP2/3-21G	−1.88	719.14	−1525.6
CAM-B3LYP/3-21G	−1.82	719.27	−1671.9
LC-BLYP/3-21G	−1.77	702.79	−1193.4
B3LYP/3-21G	−1.91	758.63	−4484.7
CurDFT/DZP	−2.09	672.05	−5378.5
LB94/DZP	−2.09	901.25	−10291.0
RevPBEx/DZP	−2.42	900.59	−15196.0
GRAC/DZP	−2.64	926.19	−19816.0
PW91/3-21G	−2.19	819.73	−20125.6
KT2/DZP	−2.79	939.00	−22050.0
LDA/3-21G	−2.32	830.09	−22487.0
KT1/DZP	−2.81	948.14	−22541.0
KLI/DZP	−3.65	975.11	−83807.0

[a] All values are given in atomic units.

and electroluminescent components;[10,11,15] films of TPhA have been used in organic-light-emitting-diodes (OLEDs).[16] In all three dyad systems a pyrrolidine unit is incorporated into the skeleton of the [60]fullerene (using the well-established 1,3-dipolar cycloaddition reaction of azomethine ylides[17]). Here we study how modification of the chromophore influences the non-resonant first and second hyperpolarizability.

Apart from non-resonant properties, resonant two-photon absorption (TPA) is also of interest. Although TPA was predicted by Maria Göppert-Mayer in the early 1930s,[18] it has only recently attracted significant attention.[19−27] This is due to various optical applications, including optical limiting[28] and optical data storage.[29] On the basis of numerous theoretical and experimental investigations, certain structure−property relationships have been established for TPA in conjugated organic molecules.[19,20,26] However, only a small number of studies have been devoted to functionalized fullerenes.[30] It has been observed experimentally that TPA cross sections of [60]fullerene−chromophore dyads can be as large as 10^4 GM (1 GM = 1×10^{-50} cm^4·s·photon^{-1}·molecule^{-1}).[31] However, the measurements were performed with pulses of nanosecond duration, and the observed TPA includes contributions from secondary processes.[31] Hence, we also want to calculate and analyze the TPA of **1**, **2**, and **3** as a function of wavelength.

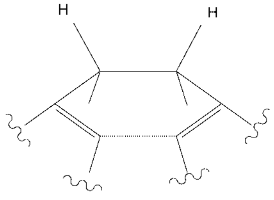
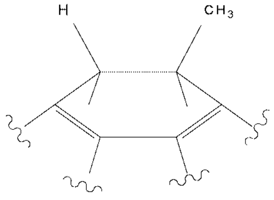
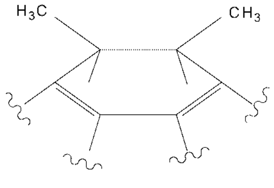
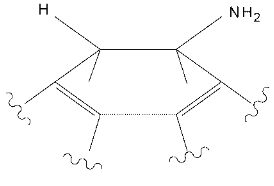
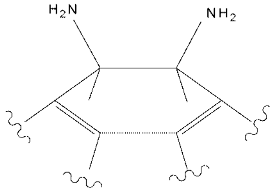
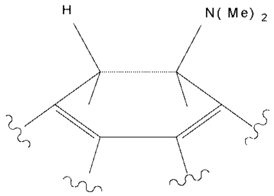
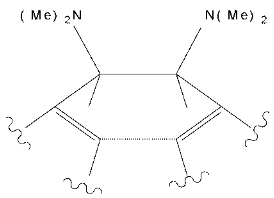
The performance of various theoretical approaches for calculation of nonlinear optical properties has been examined extensively.[32] It is desirable to apply coupled cluster methods wherever possible.[33] However, this level of theory is not a practical choice for large systems. Even the computationally less intensive MP2 method is too demanding for the systems under consideration here except for benchmarking purposes. An alternative is density functional theory, which accounts for electron correlation much more efficiently than wave function treatments. It has been recognized, however, that the majority of exchange-correlation functionals fail to correctly predict polarizabilities and hyperpolarizabilities of chain-like molecules.[34,35] Long-range corrected (LRC) functionals have been proposed recently to alleviate this deficiency. In this article, we shall refer to such methods as LRC-DFT and, in particular, we

TABLE 1: Geometrical Parameters of 1 Calculated Using the PM3 Method and at the B3LYP/6-31G(d) Level of Theory[a]

method	C−C (6−6)	C−CH$_2$	C−CHR	N−CH$_2$	N−CHR	N−CH$_3$	N′−CH$_3$	∠CH$_2$NCH$_3$	∠CN′CH$_3$	∠C1N′C2C3
PM3	1.584	1.537	1.556	1.486	1.500	1.474	1.466	113.8	121.0	149.4
B3LYP	1.611	1.556	1.558	1.452	1.463	1.457	1.447	112.7	125.6	177.8

[a] N′ refers to the nitrogen atom located in carbazole moiety. All other parameters refer to the pyrrolidine ring. Distances are given in Å and angles in degrees.

TABLE 4: Values of the Dipole Moment (μ), Average Linear Polarizability, ($\bar{\alpha}$), and Average First Hyperpolarizability ($\bar{\beta}$) for Several Model Systems[a]

Label	Molecule	μ	$\overline{\alpha}$	$\overline{\beta}$	Method
9		1.00	449.23	-29.0	HF/6-31G(d)
		0.92	479.65	-58.2	BLYP/6-31G(d)
10		1.07	461.00	-18.6	HF/6-31G(d)
		0.98	493.24	-36.0	BLYP/6-31G(d)
11		1.18	472.26	-3.4	HF/6-31G(d)
		1.10	506.32	12.45	BLYP/6-31G(d)
12		1.09	457.12	-29.3	HF/6-31G(d)
		1.01	490.18	81.9	BLYP/6-31G(d)
13		1.21	465.04	-7.5	HF/6-31G(d)
		1.19	501.79	277.2	BLYP/6-31G(d)
14		1.11	481.76	-64.3	HF/6-31G(d)
		1.00	520.46	1019.1	BLYP/6-31G(d)
15		1.33	512.28	-74.8	HF/6-31G(d)
		1.28	562.06	3046.5	BLYP/6-31G(d)

[a] All values are given in atomic units.

will examine the suitability of the LC-BLYP[36−38] and CAM-B3LYP[39] variants for the systems/properties at hand. LRC-DFT has been used to calculate nonlinear optical properties for a number of systems[37,38,40−42] but we are not aware of any studies

TABLE 5: Values of Dipole Moment (μ) and First- (α), Second- (β) and Third-Order Polarizability (γ) for 1, 2, and 3[a]

property	method	1	2	3
μ_x	HF/3-21G	−1.79	1.09	−1.29
	MP2/3-21G	−1.88	1.00	−1.25
	LC-BLYP/3-21G	−1.77	0.94	−1.22
	PM3	−1.30	0.86	−1.02
α_{xx}	HF/3-21G	681.87	859.68	1051.74
	MP2/3-21G	719.14	867.34	1079.56
	LC-BLYP/3-21G	702.79	874.92	1091.88
	PM3	671.91	858.72	1061.88
β_{xxx}	HF/3-21G	−674.0	664.1	−4552.2
	MP2/3-21G	−1525.6	985.4	−8267.3
	LC-BLYP/3-21G	−1193.3	874.9	−7457.4
	PM3	−1028.2	1373.7	−7400.9
γ_{xxxx}	HF/3-21G	171729	596479	1542361
	MP2/3-21G	384606	988307	3103560
	LC-BLYP/3-21G	291518	826348	2655793
	PM3	261749	1073875	3051099

[a] All values are given in atomic units.

on organofullerenes. More conventional functionals are also used for comparison purposes.

In the present contribution we compute both electronic (section 3.2) and vibrational (section 3.4) contributions to the non-resonant (hyper)polarizability of the [60]fullerene derivatives mentioned above and study their one- and two-photon absorption as well. We also relate these linear and nonlinear optical properties to their electronic structure (section 3.3) in order to build a basis for the rational design of new [60]fullerene derivatives suitable for photonic applications.

2. Computational Methods

Geometry optimizations were performed using the semiempirical PM3 Hamiltonian[43,44] and the B3LYP/6-31G(d) method. All stationary points were confirmed to be minima by evaluation of the Hessian. The calculation of the linear and nonlinear optical properties is described in the following sub-sections. In order to speed up computations the fast multipole method (FMM),[45−47] as implemented in Gaussian 03,[48]has been used wherever applicable.

2.1. Definition of Static Electric Dipole Properties. In the presence of moderate uniform static electric fields, in one or more Cartesian directions, the total molecular energy can be expressed as a Taylor series:

$$E(F) = E(0) - \mu_i F_i - \frac{1}{2!}\alpha_{ij}F_iF_j - \frac{1}{3!}\beta_{ijk}F_iF_jF_k - \frac{1}{4!}\gamma_{ijkl}F_iF_jF_kF_l - ..., \quad (1)$$

where $E(0)$ denotes the energy without external perturbation; the Greek symbols $\alpha, \beta, ...,$ label tensor quantities; and the subscripts indicate Cartesian directions. This expansion (1) conforms to the so-called T-convention[49] and is employed here for determination of the static linear polarizability (α), first hyperpolarizability (β) and second hyperpolarizability (γ). The Einstein summation convention is used here. The average (hyper)polarizabilities are defined in the following way:[32]

$$\bar{\alpha} = \frac{1}{3}\sum_{i=x,y,z}\alpha_{ii} \quad (2)$$

$$\bar{\beta} = \sum_{i=x,y,z}\frac{\mu_i\beta_i}{|\vec{\mu}|} \quad (3)$$

where

$$\beta_i = \frac{1}{5}\sum_{j=x,y,z}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (4)$$

and

$$\bar{\gamma} = \frac{1}{5}\sum_{ij=x,y,z}\gamma_{iijj} \quad (5)$$

Within the clamped nucleus approximation, the (hyper)polarizabilities can be divided into two parts, namely electronic and vibrational:[50]

$$P = P^e + P^{vib} \quad (6)$$

with[51]

$$P^{vib} = P^{nr} + P^{curv} \quad (7)$$

Here we compute the nuclear relaxation contribution, P^{nr}, to α^{vib} and β^{vib}. This term can be identified with lower-order vibrational terms of Bishop−Kirtman perturbation theory approach. P^{nr} is typically the larger of the two terms on the right-hand side of Eq. (7). In the above partitioning scheme the zero-point vibrational averaging contribution is part of the curvature term, P^{curv}. It is usually quite small and is not computed here.[52,53]

2.2. Static Electronic Contributions. Numerical differentiation of the total energy with respect to the static electric field(s), at the equilibrium geometry, allows for determination of the electronic contribution to the expansion coefficients in eq 1. The diagonal tensor components, for example, can be determined as:[54]

$$\mu_i F_i = -\frac{2}{3}[E(F_i) - E(-F_i)] + \frac{1}{12}[E(2F_i) - E(-2F_i)] \quad (8)$$

$$\alpha_{ii}F_i^2 = \frac{5}{2}E(0) - \frac{4}{3}[E(F_i) + E(-F_i)] + \frac{1}{12}[E(2F_i) + E(-2F_i)] \quad (9)$$

$$\beta_{iii}F_i^3 = [E(F_i) - E(-F_i)] - \frac{1}{2}[E(2F_i) + E(-2F_i)] \quad (10)$$

$$\gamma_{iiii}F_i^4 = -6E(0) + 4[E(F_i) + E(-F_i)] - [E(2F_i) + E(-2F_i)] \quad (11)$$

Although numerical calculation of μ and α strictly requires only two field-dependent energies, the use of four points as in eqs 8

TABLE 6: Comparison of Average Static Linear and Nonlinear Optical Properties of 1, 2, and 3 with the Isolated Chromophores 5, 6, and 7[a]

	method	1	5	2	6	3	7
$\bar{\alpha}$	PM3	591.89	120.75	679.70	202.92	817.79	336.95
$\bar{\beta}$	PM3	546.6	156.8	521.5	84.9	1746.2	794.4
$\bar{\gamma}$	PM3	135377	26794	307890	138123	730346	454142

[a] All values are given in atomic units.

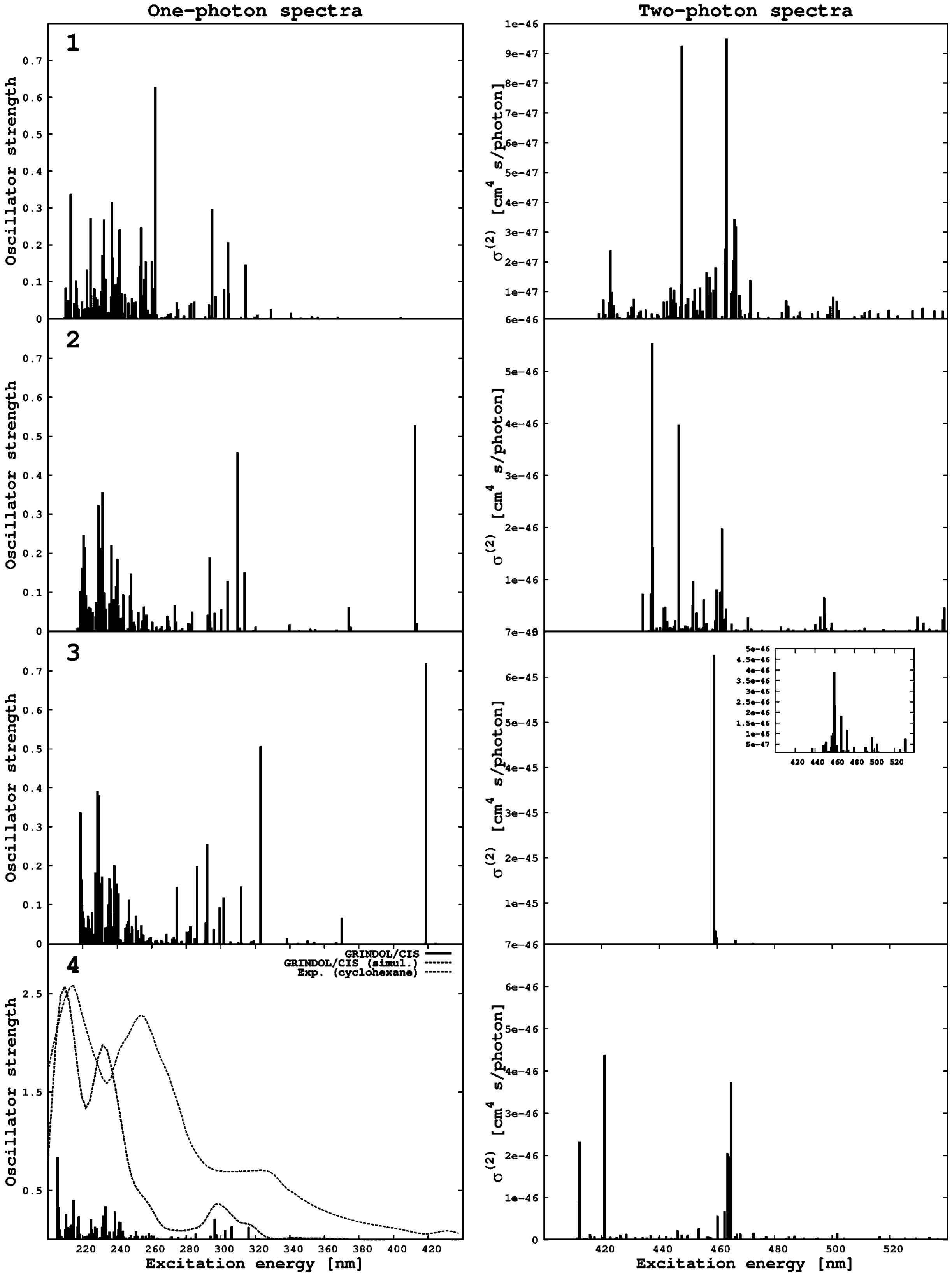


Figure 3. One- and two-photon excitation spectra for molecules **1**−**4**. The inset figure presents the TPA spectrum at reduced scale so that the weaker transitions can be seen.

and 9 reduces numerical error due to the contamination by higher-order derivatives. Such contamination is possible for β and γ. That problem was avoided by using sufficiently weak fields and the results were randomly verified by comparing with numerical differentiation of the analytical dipole moment and/or the linear polarizability obtained using the same fields.

Calculations of the electronic contribution to (hyper)polarizabilities using Hartree−Fock and second-order Møller−Plesset perturbation theory (MP2) were performed using the Gaussian 03 program,[48] while for the semiempirical calculations we used the MOPAC 2007 package.[55] Density functional theory computations were performed using Gaussian 03 (B3LYP, PW91, LDA),[48] ADF (current DFT, LB94, RevPBEx, GRAC, KT1, KT2, KLI),[56] Dalton (CAM-B3LYP),[57] and GAMESS US (LC-BLYP).[58] We used linear scaling approaches for calculations of nonlinear optical properties as implemented in the ADF package.[56] All properties are expressed in atomic units. Conversion factors can be found elsewhere.[32]

2.3. Vibrational Contributions. In order to compute vibrational nuclear relaxation (NR) contributions, the field induced coordinates (FICs) approach has been employed.[59,60] The FICs are linear combinations of field-free normal coordinates associated with the change in equilibrium geometry induced by a static electric field. The value of the i th field-free normal coordinate at the field-relaxed geometry is given by:[59]

$$Q_i^F(F_x, F_y, F_z) = -\sum_a^{x,y,z} q_1^{i,a} F_a - \sum_{a,b}^{x,y,z}\left[q_2^{i,ab} - \sum_{j=1}^{3N-6}\frac{a_{21}^{ij,a}}{a_{20}^{ii}}q_1^{i,b} + \sum_{j,k=1}^{3N-6}\frac{3a_{30}^{ijk}}{2a_{20}^{ii}}q_1^{j,a}q_1^{k,b}\right]F_aF_b + \ldots \quad (12)$$

where,

$$a_{nm}^{ij\ldots ab\ldots} = \frac{1}{n!m!}\left(\frac{\partial^{(n+m)}V(Q_1, \ldots, Q_{3N-6}, F_x, F_y, F_z)}{\partial Q_i \partial Q_j \cdots \partial F_a \partial F_b \cdots}\right)_{Q=0,F=0} \quad (13)$$

and

$$q_1^{i,a} = \frac{a_{11}^{i,a}}{2a_{20}^{ii}}, \quad q_2^{i,ab} = \frac{a_{12}^{i,ab}}{2a_{20}^{ii}} \quad (14)$$

Here, in order to conform to standard practice, the indices i, j, k label normal coordinates whereas a, b, c now refer to Cartesian directions along molecular axes. This should not cause any confusion since we will use the Cartesian directions x, y, z to report our results. The quantities a_{nm} involve the nth derivative of the potential energy $V(Q, F)$ with respect to normal coordinates and the m th derivative with respect to field components. In terms of these quantities the first- and second-order FICs are defined as follows:[59]

$$\chi_1^a = -\sum_{i=1}^{3N-6} q_1^{i,a} Q_i \quad (15)$$

and

$$\chi_2^{ab} = -\sum_{i=1}^{3N-6}\left[q_2^{i,ab} - \sum_{j=1}^{3N-6}\frac{a_{21}^{ij,a}}{a_{20}^{ii}}q_1^{j,b} + \sum_{j,k=1}^{3N-6}\frac{3a_{30}^{ijk}}{2a_{20}^{ii}}q_1^{j,a}q_1^{k,b}\right]Q_i \quad (16)$$

Depending on the NLO property of interest, a small set of FICs, independent of the number of atoms in the molecule, may be employed to calculate the total NR contribution which would be obtained using all three $N - 6$ normal coordinates. For example, from the three first-order FICs (one for each Cartesian direction) one can compute the nuclear relaxation contributions to the static polarizability and first hyperpolarizability, as follows:

$$\alpha_{ab}^{nr}(0;0) = \frac{1}{2}\sum P_{ab}\frac{\partial \mu_a}{\partial \chi_1^b}\frac{\partial \chi_1^F}{\partial F_b} = [\mu^2]^{(0,0)} \quad (17)$$

$$\beta_{abc}^{nr}(0;0,0) = \sum P_{abc}\left[\frac{1}{2}\frac{\partial \alpha_{ab}}{\partial \chi_1^c}\frac{\partial \chi_1^F}{\partial F_c} + \frac{\partial^2 \mu_a}{\partial \chi_1^b \partial \chi_1^c}\frac{\partial \chi_1^F}{\partial F_b}\frac{\partial \chi_1^F}{\partial F_c} - \frac{1}{6}\frac{\partial^3 V}{\partial \chi_1^a \partial \chi_1^b \partial \chi_1^c}\frac{\partial \chi_1^F}{\partial F_a}\frac{\partial \chi_1^F}{\partial F_b}\frac{\partial \chi_1^F}{\partial F_c}\right] = [\mu\alpha]^{(0,0)} + [\mu^3]^{(1,0)} + [\mu^3]^{(0,1)} \quad (18)$$

Here P_{ab}... indicates the sum over all permutations of the indices a, b,... The superscripts in the last line of eq 18 denote the order (in perturbation theory) of electrical and mechanical anharmonicity, respectively.[61] It is also possible, using only first-order FICs, to compute the NR contribution to the frequency-dependent Pockels effect (dc−P) $\beta(-\omega; \omega, 0)$ and electric field induced second-harmonic generation (EFISH) $\gamma(-2\omega; \omega, \omega, 0)$ in the infinite optical frequency ($\omega \rightarrow \infty$) approximation. In the latter approximation the first-order corrections vanish and we are left with a double harmonic term. The same is true of the intensity-dependent refractive index (IDRI) $\gamma(-\omega; \omega, -\omega, \omega)$. More details about this method can be found elsewhere.[59,60,62]

The potential energy and electrical properties in eqs 17 and 18 were computed using the Gaussian 03 program.[48] Derivatives with respect to the FIC coordinate were obtained numerically, at the field-free optimum geometry, by applying a number of steps along the FIC vector. This was done for molecule **8**. In other cases, the nuclear relaxation contributions were estimated based on the double-harmonic oscillator approximation (which is exact for α, dc−P, and IDRI),[32,63] and, in that event, the GAMESS US package was employed.[58] In calculating vibrational contributions at a given level of theory, we were careful to use the geometry optimized by the very same method.

2.4. One- and Two-Photon Absorption (TPA). The quantity needed to describe the simultaneous absorption of two photons which, in general, have different energies ($\hbar\omega_1 \neq \hbar\omega_2$) and different polarization ($\vec{\zeta}_1 \neq \vec{\zeta}_2$) is given by the following equation:[64]

$$S_{ij}^{0F}(\vec{\zeta}_1, \vec{\zeta}_2) = \hbar^{-1}\Sigma_K\left[\frac{\langle 0|\vec{\zeta}_1\cdot\hat{\mu}_i|K\rangle\langle K|\vec{\zeta}_2\cdot\hat{\mu}_j|F\rangle}{\omega_K - \omega_1} + \frac{\langle 0|\vec{\zeta}_2\cdot\hat{\mu}_i|K\rangle\langle K|\vec{\zeta}_1\cdot\hat{\mu}_j|F\rangle}{\omega_K - \omega_2}\right] \quad (19)$$

Here $\hbar\omega_1 + \hbar\omega_2$ should satisfy the resonance condition $\omega_F = \omega_1 + \omega_2$ and $\langle K|\vec{\zeta}_1\cdot\hat{\mu}|L\rangle$ is the transition moment between electronic states K and L, respectively. Since in most experiments one source of photons is used, one can substitute $0.5\cdot\omega_F$ for the angular frequencies ω_1 and ω_2. In the case of isotropic media the averaged two-photon absorption cross section is given by

$$\langle \delta^{0F} \rangle = \frac{1}{30}\Sigma_{ij}[S_{ii}^{0F}(S_{jj}^{0F})^*\bar{F} + S_{ij}^{0F}(S_{ij}^{0F})^*\bar{G} + S_{ij}^{0F}(S_{ji}^{0F})^*\bar{H}] \quad (20)$$

where $\bar{F} = \bar{F}\ (\bar{\zeta}_1, \bar{\zeta}_2)$, $\bar{G} = \bar{G}\ (\bar{\zeta}_1, \bar{\zeta}_2)$, and $\bar{H} = \bar{H}\ (\bar{\zeta}_1, \bar{\zeta}_2)$ are the polarization variables. For two linearly polarized photons with parallel polarization, $\bar{F}, \bar{G}, \bar{H} = 2$ and the two-photon absorption cross-section is as follows:[64]

$$\langle\delta^{0F}\rangle = \frac{1}{15}\Sigma_{ij}[S_{ii}^{0F}(S_{jj}^{0F})^* + 2S_{ij}^{0F}(S_{ij}^{0F})^*] \qquad (21)$$

The comparison of the theoretically determined two-photon absorption cross section with experimental spectra is based on the following relation:

$$\sigma_{0F}^{(2)} = \frac{8\pi^3\alpha^2\hbar^3}{e^4}\frac{\omega^2 g(\omega)}{\Gamma_F/2}\langle\delta^{0F}\rangle \qquad (22)$$

where e is the magnitude of the electronic charge, α is the fine structure constant (not to be confused with the linear polarizability), $\hbar\omega$ is the energy of absorbed photons (assuming single source of photons), Γ_F is the lifetime broadening of the final state and $g(\omega)$ is the spectral line profile, which is assumed here to be a δ function. The quantities on the right-hand side of eq 19 were obtained from single excitation configuration interaction (CIS) calculations using the GRINDOL method,[78] which is based on the INDO approximation, with 2000 singly excited configurations. The same GRINDOL calculation also yields the quantities needed to obtain the one-photon absorption spectrum. As shown previously, the GRINDOL/CIS level of theory correctly predicts both one-photon spectra and nonlinear optical properties of donor−acceptor systems.[65,66] Although approximate theoretical treatments of the vibrational contribution to TPA have been presented,[67,68] as well as a more complete formulation,[69] neither has been attempted here due to computational and/or reliability considerations.

3. Results and Discussion

This section is organized as follows. First, we shall discuss the structure of the investigated systems (section 3.1). Then the electronic contributions to linear polarizability, and first and second hyperpolarizability are presented in section 3.2. In the following section we analyze one- and two-photon absorption spectra (section 3.3) and, finally, the discussion of vibrational contributions to the (hyper)polarizabilities is given in section 3.4.

3.1. Structure of Investigated Molecules. *Ab initio* calculation of optimized geometries for the systems investigated here is computationally demanding, especially since we want to evaluate the Hessian to confirm that the stationary point is a minimum. Thus, the semiempirical PM3 method was used for this purpose. In order to assess the reliability of the PM3 structures, we optimized the geometry of **1** (Figure 2) at the B3LYP/6-31G(d) level of theory as well. The comparison of PM3 and B3LYP results reveals only minor changes in the bond distances of the fullerene moiety, i.e. the carbon−carbon (hexagon−pentagon) and (hexagon−hexagon) bond length differences do not exceed 0.01 Å and 0.012 Å, respectively. The values of selected geometrical parameters for **1** are listed in Table 1. They are in reasonable agreement. Perhaps the most significant difference between PM3 and B3LYP/6-31G(d) occurs for the N′−CH_3 group of the carbazole moiety. Fortunately, this difference does not have a significant effect on the linear and nonlinear optical properties as seen below. No experimental structure is available for **1**.

In Table 2 we present values for the electronic dipole moments and average (hyper)polarizabilities of **1** calculated at the HF/6-31G(d) level of theory for the structures obtained by the two methods discussed above. The difference in property values is not substantial as far as the purposes of this study are concerned. Thus, the structures of all investigated molecules were optimized using the PM3 method, except for evaluation of vibrational contributions to α and β, in which case the structure and property derivatives must be obtained by the same method as previously noted. It should be mentioned that we consistently use the so-called standard orientation[70] which is presented for molecules **1**−**3** in Figure 2.

3.2. Electronic Contributions to (Hyper)Polarizabilities. In this section, we discuss the electronic contributions to α, β and γ. In particular, two aspects will be considered in detail: (1) the reliability of DFT results obtained using various exchange-correlation functionals and (2) the relation between the structure and non-linear optical properties of the molecules studied here.

Our calculated results for the largest diagonal, *i.e.*, x, component of the static μ, α, and β of molecule **1** are presented in Table 3 for various DFT functionals; HF and MP2 values are also given for comparison. The DFT functionals were tested using either a 3-21G or DZP basis. It is now well-recognized that conventional functionals tend to strongly overshoot the magnitude of longitudinal electrical property values in conjugated chain-like molecules.[34,35,71−73] Hence, the very large values, compared to Hartree−Fock or MP2 or the (nonconventional) CAM-B3LYP and LC-BLYP functionals, as reported in Table 3, should probably not be surprising. The overshoot for β is especially noticeable. Although the DZP basis is not quite the same as 6-31G(d) they are similar enough to make valid comparisons.

As far as the non-conventional functionals are concerned, KLI[74] has been found to yield substantial improvement for α and γ of molecular hydrogen chains[71] with bond length alternation, although deficiencies still remain in comparison to, say, the optimized effective potential (OEP).[76] Since OEP is, in principle, equivalent to Hartree−Fock, we can compare with the latter. In that event the overshoot we obtain for the KLI β is quite striking. The non-conventional current−DFT (cDFT) approach[75] has previously proved successful for α of π-conjugated molecules,.[73] However, it has difficulty in this case with μ and, especially, with β. On the other hand, the recently developed LRC functionals CAM-B3LYP[39] and LC-BLYP,[36−38] which use exact Hartree−Fock exchange at long-range together with more conventional functionals at short-range, successfully cure the overshoot problem.

Judging by the comparison between Hartree−Fock and MP2 (as well as the two LRC functionals) the effect of electron correlation on β appears to be important. This is consistent with what has been found for a number of charge transfer molecules. Extending the basis set from 3-21G to 6-31G(d) has a smaller, though still significant, effect on both the HF and MP2 values of β. We have not attempted here to use basis sets containing diffuse functions in order to avoid possible linear dependency problems. Thus, we expect the values of molecular (hyper)polarizabilities to be underestimated.

In order to investigate the connection between the overshoot for β obtained by conventional DFT and the donor−acceptor character of the dyad, we performed calculations for several systems obtained by saturating a hexagon−hexagon bond of the [60]fullerene moiety with hydrogen atom and a simple donor group (or two) (see Table 4) attached to the [60]fullerene moiety. Although these systems may not adequately model molecules **1**−**3** the results turn out to be very suggestive. In these calculations BLYP was used as a representative conventional functional and comparison was made to HF, which does not suffer from the overshoot problem. The additive substituents were selected according to increasing Hammett σ_p constant, which may be used as a measure of their electron donating capabilities.[77]

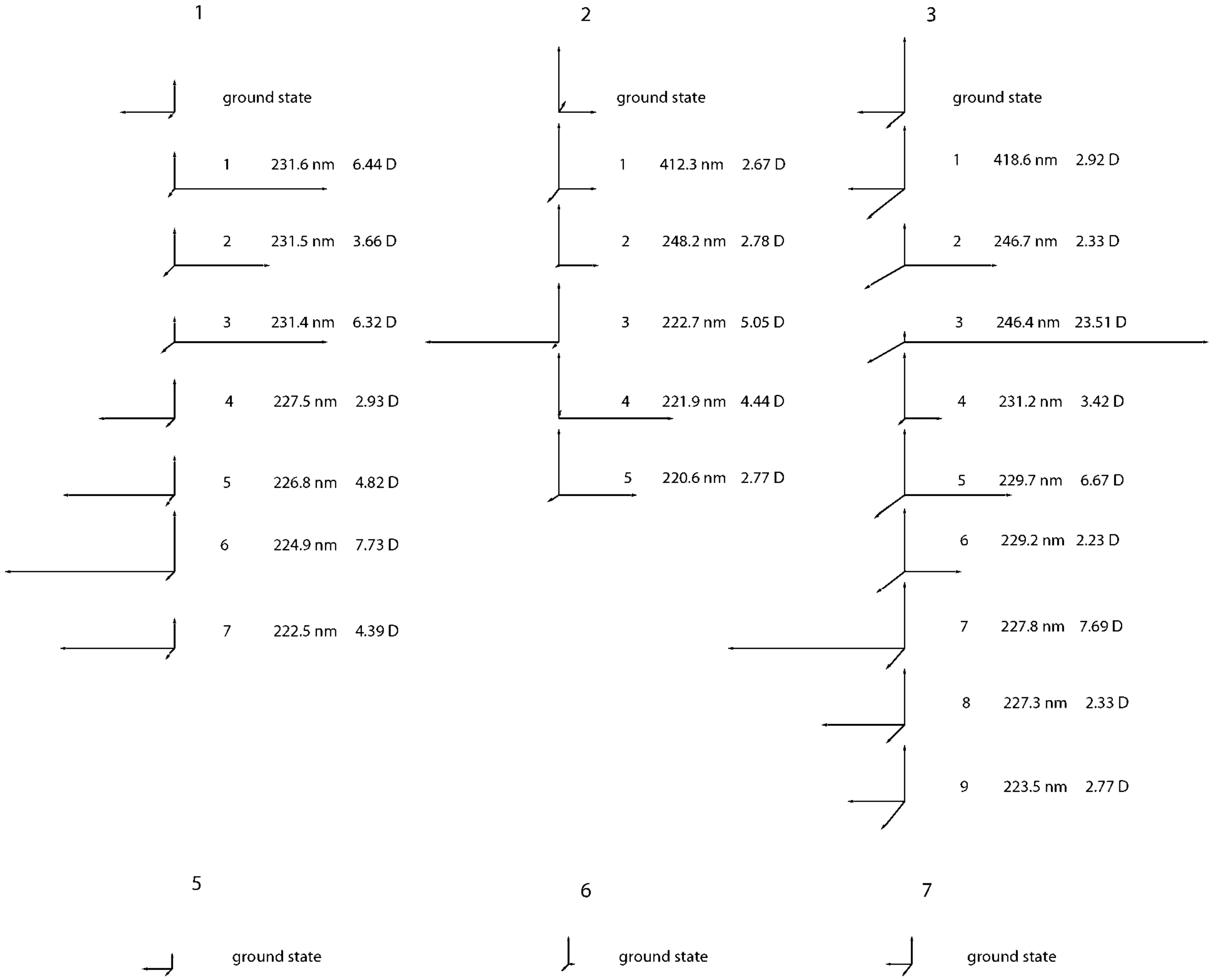


Figure 4. Schematic representation of dipole moment components in the ground and selected excited states (see text for explanation) for **1**, **2**, and **3**, respectively. Ground state dipole moment components for **5**, **6**, and **7** are presented as well. The components refers to the orientation of molecules presented in Figure 2. Shown also are the excitation energies and the magnitude of the difference in dipole moment between the given excited-state and the ground state.

TABLE 7: Electronic and Vibrational Contributions to Molecular (Hyper)Polarizabilities Calculated at the HF/6-31G Level of theory for 1, 2, 3, 5, 6, 7, and 8[a]

	1	5	2	6	3	7	8
$\bar{\alpha}^{nr}$	29.2	4.0	42.2	4.3	119.0	86.6	11.8
$\bar{\alpha}^{e}$	609.6	127.0	695.2	205.7	836.3	339.5	458.6
$[\bar{\mu}\bar{\alpha}]^{(0,0)}$	3037.0	50.1	5660.1	74.9	4590.4	7329.1	160.8
$\bar{\beta}^{nr}(-\omega;\omega,0)_{\omega\to\infty}$	1012.0	16.7	1886.7	25.0	1530.1	2443.0	53.6
$\bar{\beta}^{e}$	288.2	89.9	−51.8	−25.5	835.8	268.0	−4.0
$\bar{\gamma}^{nr}(-\omega;\omega,-\omega,\omega)_{\omega\to\infty}$	48637	5702	155719	25818	293915	133909	19437
$\bar{\gamma}^{e}$	67158	12189	151985	56683	361605	17552	26880

[a] All values are given in atomic units.

On the basis of the data in Table 4, one fact clearly emerges. For the sequence of molecules **9**, **10**, **12** and **14**, ordered according to increasing Hammett σ_p of the donor substituent,[77] the ratio of the BLYP and HF values for $\bar{\beta}$ increases monotonically and becomes quite large for the strongest donors. Furthermore, a very similar pattern is seen for the doubly substituted [60]fullerene derivatives.

The results of calculations for the static electric dipole properties of molecules **1**, **2** and **3** are presented in Table 5. Our aim here is to validate the PM3 procedure. For this purpose, we focused on the diagonal x-component. This component is the largest for α, β, and γ, though not necessarily for μ. The overall agreement between PM3 and LC-BLYP/3-21G is satisfactory from our point of view and both procedures are reasonably consistent with MP2/3-21G. As implied above this will not be altered by choosing a larger basis set. Thus, we shall use values of $\bar{\alpha}$, $\bar{\beta}$ and $\bar{\gamma}$ calculated using PM3 as the basis for further analysis.

PM3 values for the averaged static electric properties of **1**, **2**, and **3** are shown in Table 6 along with the corresponding isolated chromophores **5**, **6**, and **7**, respectively. The chromophore dyad values are considerably larger although, as might be expected, this effect decreases as the length of the isolated chromophore increases. Nonetheless the general trends for both sets of molecules parallel one another. In both cases the magnitude of $\bar{\beta}$ is similar for **1** (**5**) and **2** (**6**) while the value for

3 (**7**) is much larger. For $\bar{\alpha}$ and $\bar{\gamma}$ there is a systematic increase along the sequence: **1** → **2** → **3** (**5** → **6** → **7**).

3.3. One- and Two-Photon Absorption Spectra. One- and two-photon absorption spectra were calculated using the GRINDOL[78] CIS method as described in section 2.4. This technique has been proven to provide reliable prediction of one-photon spectra of organic compounds.[79] Theoretically determined one-photon spectra of isolated **1**, **2**, **3**, and **4** are presented in Figure 3. The spectrum of **4** measured in cyclohexane by Maggini et al.[80] is also presented in Figure 3. Our semiempirical calculations (without solvent correction) agree fairly well with the experimental data.

Comparison of spectra of **4** and **1** reveals the existence of a very intense peak (oscillator strength greater than 0.6) in the spectrum of **1**, located at 262 nm, which is not present in the spectrum of **4**. An analysis of the CI vectors reveals that this is a $\pi \rightarrow \pi^*$ transition that occurs in the pyrrolidine ring of the carbazole moiety.

In the case of compounds **2** and **3** one obtains very intense transitions at 412 and 309 nm for **2** and 418 and 323 nm for **3**. The calculated absorption band maxima for **3** are in good agreement with the experimental values of 436 and 310 nm for the chromophore in CH_2Cl_2.[14] The authors attributed these to intramolecular $\pi \rightarrow \pi^*$ transitions from the TPhA (donor) to the benzothiadiazole (acceptor) moiety.[14] The results of our calculations fully support this assignment. No experimental data has been reported for compound **2**.

For molecule **3** we also calculated one-photon spectra with the aid of time-dependent density functional theory using B3LYP functional and 6-31G(d) basis set. The most intense transition is predicted at 2.186 eV (567 nm), which is significantly shifted to higher wavelength from both the measured and GRINDOL values. The large disagreement with experiment is consistent with the fact that charge transfer excitations are poorly described by B3LYP calculations.[40] Finally, we note that the spectrum below 250 nm is connected with excitations localized mainly in the [60]fullerene moiety as may be seen by comparing with our Figure 3 which also contains the experimental data reported by Maggini et al.[80] The same is true for the other three molecules.

Figure 4 presents the dipole moment components of **1**, **2** and **3** in their ground-state as well as in selected excited states. The dipole moments were calculated as expectation values based on the CIS wave function of a given singlet excited-state determined using the GRINDOL method. The computations were performed for molecules oriented as presented in Figure 2. We include only states for which $\Delta\mu = \mu_e - \mu_g > 2$ D (0.787 au) and $f > 0.05$, where f, μ_e, and μ_g denote oscillator strength, excited-state, and ground-state dipole moment, respectively. In cases where a single charge-transfer state is dominant the quantities $\Delta\mu$ and f are the key parameters determining the first hyperpolarizability[6] as well as the two-photon absorption cross section.[81] From Figure 4 we see that it is the x component of $\Delta\mu$ that achieves particularly large values. That component points in the same direction (i.e., from the [60]fullerene moiety toward the chromophore) for **1**, **2**, and **3**. We also present in Figure 4 the ground-state dipole moment components for the chromophores **5**, **6**, and **7** at the same orientation. By comparing the chromophore to the corresponding dyad it is clear that the [60]fullerene serves as an electron withdrawing moiety in the ground-state of all three molecules. On the other hand, the [60]fullerene moiety can act as an electron-donating group in excited states.[82] Indeed, it is seen from Figure 4, that in some excited states of **1**, **2**, and **3**, the x component of the dipole moment changes sign and has a large increase in magnitude. This is indicative of the fact that the [60]fullerene moiety is donating electrons to the carbazole-based and 2,1,3-benzothiadiazole-based units.

The two-photon absorption spectra of the investigated molecules is presented in Figure 3. These plots were prepared assuming that the lifetime broadening of all states is 6000 cm^{-1}. This choice satisfactorily reproduced the experimental spectrum of the 2,1,3-benzothiadiazole derivative.[83] Values of the TPA cross-sections are on the order of 10^4 GM. The largest peaks in the TPA spectrum appear in the region 400−470 nm, corresponding to the strongest one-photon absorptions of the [60]fullerene moiety which occur in the region 200−235 nm. From Figure 3 we see that the largest TPA cross section for **3** is almost an order of magnitude greater than that of the other systems. Likewise, the Re $\bar{\gamma}$ value for **3** (as opposed to Im $\bar{\gamma}$, which determines TPA) is much larger than the corresponding value for **1** and **2** (see Table 6).

3.4. Vibrational Contributions to Electric (Hyper)Polarizabilities. In this section, we present our results for vibrational contributions to the average (hyper)polarizabilities calculated at the HF/6-31G level of theory for **1**, **2**, **3,** and **8** as well as for the chromophores **5**, **6**, and **7**. As mentioned previously, the geometries used were optimized at the same level of theory, i.e. HF/6-31G. Due to computational limitations these calculations were limited to the double harmonic approximation except for **8**. For all the properties considered here except static β the NR treatment is identical to the double harmonic approximation. For the static β a first-order perturbation correction due to electrical and mechanical anharmonicity is included in NR as well. For **8** the NR calculations were carried out fully numerically.

In the case of **8**, we focused on the Cartesian x direction to obtain a preliminary assessment of the magnitude of the NR contribution. This direction, which is parallel to the N−H bond of the pyrrolidine ring, corresponds to the largest (in magnitude) diagonal component of the purely electronic β at the Hartree−Fock level of theory. It was found that the static $\alpha_{xx}^{nr} = 11.78$ au is much smaller than the electronic counterpart (501.28 au). However, the opposite is true for the static first hyperpolarizability since the electronic β_{xxx}^{e} is -35.8 au whereas $\beta_{xxx}^{nr} = -608.7$ au. The contribution of the harmonic term $[\mu\alpha]^{(0,0)}$, although already larger than β^e, is only 128.7 au and, thus, it is clear that the first-order anharmonic terms $[\mu^3]^{(0,1)}$ and $[\mu^3]^{(1,0)}$ are much more important. Adopting the infinite optical frequency approximation,[60] which is known to be accurate at typical measurement frequencies, $\beta_{xxx}^{nr}(-\omega; \omega, 0)_{\omega\rightarrow\infty}$ is $^1/_3$ the static double harmonic value or 42.9 au. Within the same infinite optical frequency approximation $\gamma_{xxxx}^{nr}(-2\omega; \omega, \omega, 0)_{\omega\rightarrow\infty} = 1/4[\mu\beta]^{(0,0)} = -40$ au. In this case the value is quite small compared to the electronic $\gamma_{xxxx}^{e} = 40201$ au.

The vibrational contributions for **1**, **2**, **3**, **5**, **6**, **7**, and **8**, calculated using the double-harmonic oscillator approximation, are presented in Table 7. For β the double harmonic approximation is meaningful as far as the dc−Pockels effect is concerned, but is too crude an approximation to be useful for the static β as we have seen. Thus the quantity $[\mu\alpha]^{(0,0)}$ is listed in the table solely for convenience; it is exactly three times the dc−Pockels β. The nuclear relaxation contribution to γ for the intensity dependent refractive index process is also given in Table 7 together with the electronic contributions to the second hyperpolarizability. The results reported in Table 7 were obtained seminumerically, i.e. second derivatives of the energy (vibrational force constant matrix) were obtained by differentiation of analytical first derivatives. Thus, the comparison of these results with those discussed above may be additionally used as a reference to assess the magnitude of the numerical errors. The difference in the x component of the $[\mu\alpha]^{(0,0)}$ term was found to be 11% and much smaller for $[\mu^2]^{(0,0)}$.

From Table 7 the average static vibrational polarizability of **1** and **2** are similar in magnitude whereas the value for **3** is several times larger. For the latter, the chromophore **7** makes the dominant contribution. In each case, however, the vibrational contribution is small compared to the electronic term. The three molecules **1**, **2**, and **3** give similar values for the dc−Pockels effect and the overwhelmingly dominant contribution in the case of **1** and **2** arises because of the additional presence of the [60]fullerene moiety. Furthermore, the averaged vibrational term is substantially larger than the corresponding static electronic first hyperpolarizability at the HF/6-31G level. Based on the preliminary calculations for molecule **8** the total static vibrational contribution may even be much more important as compared to the electronic term. Obviously, it should be borne in mind that the effect of electron correlation, which has not been considered in the present study, could significantly reduce the calculated vibrational value.[84,85] The same is true of the second hyperpolarizability. In that event the nuclear relaxation contribution to $\gamma^{nr}(-\omega; \omega, -\omega, \omega)_{\omega\to\infty}$ is either comparable to the pure electronic term or a bit smaller as it is in the case of molecule **3**, which has the largest value of this property. The values of static γ^{nr} are expected to be far larger than these for the IDRI process.

4. Conclusions

In this paper we have performed an extensive analysis of electronic and vibrational contributions to molecular (hyper)-polarizabilities for several recently synthesized [60]fullerene derivatives. It has been found that the [60]fullerene moiety, acting as an electron acceptor in the ground electronic state, significantly enhances the average static (hyper)polarizabilities. Modification of the [60]fullerene−benzothiazole system by adding a triphenylamine moiety (molecule **3**) increases the average static electronic first and second hyperpolarizabilities by roughly a factor of 3 and 2 respectively. The same is true for the major diagonal component except that the factors are even larger. On the basis of HF/6-31G calculations, the vibrational nuclear relaxation contribution to the dc−P β is substantially larger than the static electronic value for all [60]fullerene−chromophore dyads that were studied while the IDRI γ is comparable to the static electronic value. The vibrational efects are enhanced for static properties (as compared to frequency-dependent hyperpolarizabilities). At the double harmonic level of approximation the static vibrational β is three times larger than for dc−P and the results obtained for **8** indicate that anharmonicity contributions may dwarf the double harmonic term for the other studied molecules. Clearly, the role of anharmonicity in the vibrational NLO properties of organofullerenes deserves further attention.

The especially large second electronic hyperpolarizability of molecule **3** is reflected in its large two-photon absorption in the 400−470 nm region, which corresponds to the strongest one-photon absorption (200−235 nm region) of the [60]fullerene moiety. Large absorption intensities are associated, at least in part, with the fact that the [60]fullerene moiety switches from being an electron acceptor in the ground-state to an electron donor in certain excited states.

Due to the size of the molecules studied here the computational methods employed were necessarily restricted. In order to obtain reliable results extensive calculations were carried out using a hierarchy of methods including HF, MP2 and DFT as well as semiempirical techniques (PM3 and GRINDOL). Linear scaling approaches were also utilized to lower the computational cost. We found that the effect of electon correlation on β is important. However, DFT calculations using current DFT, KLI, and a wide variety of conventional functionals all substantially overestimate β. Only the recently developed long-range corrected functionals were successful. Further exploration using several model [60]fullerenes revealed that the large overshoot is connected with the electron-donating capability of the substituent.

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