

Static and dynamic first hyperpolarizabilities of azo-enaminone isomers

T.L. Fonseca ^{a,*}, M.A. Castro ^a, H.C.B. de Oliveira ^b, S. Cunha ^c

^a Instituto de Física, Universidade Federal de Goiás, 74001-970 Goiânia, Goiás, Brazil

^b Unidade Universitária de Ciências Exatas e Tecnológicas, Universidade Estadual de Goiás, 459, 75001-970 Anápolis, Goiás, Brazil

^c Instituto de Química, Universidade Federal da Bahia, 40170-290 Salvador, Bahia, Brazil

Received 16 April 2007; in final form 29 May 2007

Available online 8 June 2007

Abstract

The linear polarizabilities and first hyperpolarizabilities of two geometrical isomers (*Z*, *E*) of donor–acceptor azo-enaminones have been calculated, taking into account frequency dispersion effects, through CPHF method. Static results were also obtained at the MP2 level and correlated dynamic values were estimated using the multiplicative correction scheme. Our results show that the diagonal component of the first hyperpolarizability of *E* isomers is enhanced with increasing donor strength. Dispersion effects have a marked influence for the standard frequencies considered here ($\omega = 0.0239$ and 0.0428 a.u.), specially for second harmonic generation.

© 2007 Elsevier B.V. All rights reserved.

1. Introduction

Molecular materials exhibiting quadratic nonlinear optical (NLO) have been object of intense research due to potential applications in various photonic technologies [1–4]. Among the NLO organic chromophores, an interesting class of NLO molecules with large first hyperpolarizability are the so-called donor–acceptor systems. In these organic chromophores the quadratic NLO properties, characterized by first hyperpolarizabilities, can be modulated by varying the asymmetric polarization induced by incorporation of different donor–acceptor groups.

Enaminones are chemical substances that present a conjugated system of the type $N=C=C-C=O$ with different geometric forms [5,6]. The NLO molecules studied here, namely azo-enaminones, can be obtained by incorporation of an azo group to the $N=C=C-C=O$ conjugated system. Azo-enaminone derivatives have been synthesized from the azo coupling between quinone diazides and acyclic enaminones [7,8] or more recently from the coupling of diazonium salts and enaminones [9–12]. An attractive aspect

of these latter compounds is that they are more flexible, as regards structural modifications, than those synthesized by quinone diazide route. These compounds have a planar molecular architecture favored by the intramolecular hydrogen bonds involving the azo group [7,8]. Furthermore, structural studies based on multinuclear magnetic resonance NMR revealed that azo-enaminone derivatives can exist in $CDCl_3$ solution in the form of two geometrical isomers (*Z*, *E*), due to an unusually low rotational barrier around the $C=C$ double bond [9]. In a previous study [13], we have examined the isomerization effects on the static polarizabilities of these new azo-enaminones synthesized by diazonium salt route as well as some azo-enaminones synthesized by quinone diazide route. Our *ab initio* quantum mechanical calculations showed that the relative orientation of donor groups in *p*-nitro azo-enaminones has an important impact on the magnitude of the first hyperpolarizability. In addition, it has been shown that *Z* isomers are more stable than the *E* isomers by a small amount of energy which do not reach 3 kcal/mol.

The present Letter reports *ab initio* coupled perturbed Hartree–Fock (CPHF) calculations of the frequency dependent NLO properties of azo-enaminone isomers as function of the strength of the electron-donor. We examine

* Corresponding author. Fax: +55 62 521 1014.
E-mail address: tertius@if.ufg.br (T.L. Fonseca).

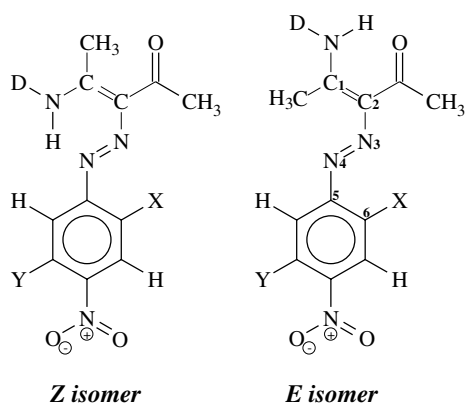


Fig. 1. Molecular structures of the azo-enaminone isomers studied in this work (see also Table 1).

Table 1
Labels of the azo-enaminone isomers presented in Fig. 1

Compounds	Substituents		
	D	X	Y
1A	H	H	H
1B	CH ₃	H	H
1C	C(CH ₃) ₃	H	H
2A	H	OH	H
3A	H	H	Cl
4A	H	OH	Cl

the isomerization influence on the diagonal and off-diagonal components of the first hyperpolarizability of azo-enaminones placed on the yx -plane with the x -axis in the direction of the permanent dipole moment. The model systems are E and Z isomers of azo-enaminones with $-\text{NO}_2$ as the electron-acceptor group attached at *para* position of the phenyl ring and $-\text{NH}_2$ as the electron-donor group. The donor character strength is varied by the replacement of an H atom of the aminic group by substituents such as $-\text{CH}_3$ and $-\text{C}(\text{CH}_3)_3$. We have also analyzed the influence of a chlorine atom attached at the phenyl ring on the optical properties of both E and Z isomers of azo-enaminones. The NLO molecules studied in this work are displayed in Fig. 1 and specified in Table 1. Previous studies have been reported showing the importance of the dispersion contributions in order to obtain a more accurate description for first hyperpolarizability [14–23]. Effects of the nuclear motion, although not considered in this work, are expected to play important roles on the calculations of the first hyperpolarizabilities [24,25]. However, previous calculations have shown that the vibrational contributions are usually negligible for second-harmonic generation processes [25].

2. Geometry and computational details

For simplicity, we have used the optimized geometric parameters of both E and Z isomers obtained previously

at the MP2 level of theory using the 6-31G basis set [13,26]. To maintain the uniformity, the molecular structures of the E isomers with a chlorine atom attached at phenyl ring have also been optimized at the MP2/6-31G level. In comparison with previously optimized geometries [13,26], the most significant structural modification related to the inclusion of the chlorine atom in the E isomers is the lost of planarity of the molecular structure. This lost of planarity can be estimated from the dihedral angles of the atoms labeled by numbers as illustrated in Fig. 1. In compound 3A_E , for instance, the MP2/6-31G results give a conformation in which both the phenyl ring and the enaminone group are twisted with respect to the plane of the azo group by 7.69° ($\text{C}_6\text{C}_5\text{N}_4\text{N}_3$) and 5.35° ($\text{N}_4\text{N}_3\text{C}_2\text{C}_1$), respectively. In compound 4A_E the phenyl ring is coplanar to the plane of the azo group and the dihedral angle between this latter group and the enaminone group is of -12.07° ($\text{N}_4\text{N}_3\text{C}_2\text{C}_1$). Despite the loss of planarity, results obtained, but not listed here, show that the incorporation of the chlorine atom almost does not affect the other geometric parameters of these E isomers as previously reported for substituted Z isomers [26]. Here the calculations of geometry optimization were also performed using the GAUSSIAN 03 package [27].

The static and dynamic electric properties were calculated analytically using the coupled perturbed Hartree–Fock procedure, implemented in the GAUSSIAN 03 program [27]. The particular second order NLO processes considered were second harmonic generation (SHG), associated with $\beta_{\text{vec}}(-2\omega; \omega, \omega)$ [2], and electro-optical Pockels effect (EOPE), related to $\beta^{\text{K}}(-\omega; 0, \omega)$ [28]. As the dipole moment was orientated along the x -axis, these dynamic properties can be written as

$$\beta_{\text{vec}} = \beta_{\text{xxx}} + \frac{1}{3} \sum_{i \neq x} \beta_{xii} + \beta_{ixi} + \beta_{iix} \quad (1)$$

and

$$\beta^{\text{K}} = \beta_{\text{xxx}} + \frac{1}{2} \sum_{i \neq x} 3\beta_{xii} - \beta_{iix}. \quad (2)$$

Notice that these equations are in the $\mu \cdot \beta/5kT$ context [28] and that $\beta_{\text{vec}} = \beta^{\text{K}}$ for $\omega = 0$. First hyperpolarizabilities can be measured by electric-field-induced second harmonic generation (EFISH) [29,30] or hyper-Rayleigh scattering (HRS) [31]. At the MP2 level, the calculations of the static properties were performed numerically through the finite field (FF) method using field strengths of the order of ± 0.001 a.u. Equivalent results for the polarizabilities obtained using both numerical and analytical procedures at the HF level provide the numerical accuracy of the FF numerical procedure employed to calculate the MP2 NLO properties of azo-enaminones. To estimate the correlated dynamic results we have employed the multiplicative correction scheme commonly used in the literature [17–19,22,23]:

$$\beta^{\text{MP2}}(-\omega_\sigma; \omega_1, \omega_2) \approx \frac{\beta^{\text{MP2}}(0; 0, 0)}{\beta^{\text{CPHF}}(0; 0, 0)} \beta^{\text{CPHF}}(-\omega_\sigma; \omega_1, \omega_2). \quad (3)$$

In this Letter the basis set influence on the static and dynamic linear polarizability and the first hyperpolarizability is analyzed for both type of isomers by comparing the results obtained using the 6-31G basis set and the 6-31G+p augmented version of this set (extra p functions are added on the heavy atoms). Thus, the exponents used in calculations when p extra functions are added on heavy atoms are $\zeta_p = 0.03$ on carbon atoms, $\zeta_p = 0.04$ on nitrogen atoms, $\zeta_p = 0.07$ on the oxygen atom and $\zeta_p = 0.02$ on chlorine atom [26]. The choice of these exponents was determined, at the HF level, by imposing the maximization of the β_{vec} values. This criterion is justifiable because the use of relatively small basis sets tends to underestimate the values of the calculated properties [32].

3. Results and discussion

Static and dynamic CPHF and static MP2 results for the components α_{xx}, α_{yy} and α_{zz} of the polarizability and β_{xxx}, β_{xyy} and β_{xzz} of the first hyperpolarizability for the azo-enaminones **1A_E** [**1A_Z**] are quoted in Table 2. Table 3 presents MP2 static results for all azo-enaminones. Both static and dynamic properties were determined on the MP2 equilibrium geometry. As the *x*-axis was placed in the direction of the permanent dipole moment, the α and β components were calculated considering such orientation. The angle between the *x*-axis and the C₆–C₁ direction (see Fig. 1) for each molecule is shown in Table 3.

The basis set effects are discussed from results obtained using the 6-31G and 6-31G+p basis sets displayed in Table 2. The calculations for dynamic properties were performed for the standard frequencies $\omega = 0.0239$ and 0.0428 a.u., but to avoid the proliferation of number only data for $\omega = 0.0428$ a.u. were included in this table. Our findings show that for each property the static and dynamic results have a very similar basis set dependence and that the first hyperpolarizability values are more dependent of the iso-

meric form than those linear polarizability ones. The out-of-plane component α_{zz} is found to be more sensitive to the basis set effects than the in-plane components α_{xx} and α_{yy} . For instance, MP2 results show that the addition of p diffuse functions leads to further increase of α_{zz} by 47% [47%] whereas the corresponding increases of α_{xx} and α_{yy} , are, respectively, of 7% [9%] and 11% [6%]. Significant basis set effects are also observed for the first hyperpolarizability components. The use of the 6-31G+p basis set increases the MP2 values of β_{xxx} and β_{xyy} , respectively, by an amount of 12% [25%] and 23% [12%], as compared with those obtained with the 6-31G basis set.

We have also analyzed the impact of the addition of d functions on the chlorine atom. Thus, for the compounds **3** and **4**, the 6-31G+p basis set was supplemented by the addition of d extra functions with exponent $\zeta_d = 0.06$, determined by maximization of β_{vec} . Using the 6-31G+pd basis set, the β_{xxx} values (in 10^{-30} esu) obtained at the HF level for the compounds **3A_E** [**3A_Z**] and **4A_E** [**4A_Z**] are 23.79 [17.68] and 17.76 [11.57], respectively, while the corresponding 6-31G+p ones are 23.69 [17.66] and 17.73 [11.60]. These results show that the addition of d diffuse functions on the Cl atom has a negligible effect on β_{xxx} . A similar conclusion have been drawn for β_{xyy} at the HF level as well as for both components at the MP2 level.

Effects of incorporation of different functional groups on the correlated static properties are discussed from the MP2/6-31G+p results listed in Table 3. Similar conclusions would be drawn for frequency dependent properties. The results show that for **1**-type isomers the incorporation of stronger donor groups at the aminic nitrogen leads to a systematic increase of α_{xx}, α_{yy} and α_{zz} , regardless the isomer type, as a consequence of the additive nature of this property [33–35]. For instance, results for **1B_E**/**1A_E** [**1B_Z**/**1A_Z**] and **1C_E**/**1B_E** [**1C_Z**/**1B_Z**] ratios show that the α_{xx} values are enhanced by 15% [9%] and 19% [14%], respectively. In contrast, the effects of the introduction of these substituents on the hyperpolarizability are further dependent of the isomer type. For diagonal components, in particular, these effects have opposite directions for the *E* and *Z* isomers. The β_{xxx} values of the *E* isomers increase with

Table 2

Static and dynamic linear polarizabilities (in 10^{-24} esu) and first hyperpolarizabilities (in 10^{-30} esu) of isomers **1A_E** [**1A_Z**] computed using different basis sets. All calculations were performed using MP2/6-31G optimized geometry

	MP2		CPHF			
	$\omega = 0$		$\omega = 0$		$\omega = 0.0428$ a.u.	
	6-31G	6-31G+p	6-31G	6-31G+p	6-31G	6-31G+p
$\alpha_{xx}(-\omega; \omega)$	42.42 [37.40]	45.45 [40.66]	39.51 [37.48]	41.32 [39.34]	41.17 [39.07]	43.13 [41.07]
$\alpha_{yy}(-\omega; \omega)$	31.00 [36.77]	34.44 [39.07]	29.11 [31.16]	31.21 [33.03]	29.78 [31.93]	31.98 [33.89]
$\alpha_{zz}(-\omega; \omega)$	8.58 [8.65]	12.62 [12.68]	8.47 [8.54]	11.85 [11.93]	8.49 [8.56]	11.92 [12.00]
$\beta_{xxx}(-\omega; 0, \omega)$	40.60 [19.64]	45.30 [24.58]	21.31 [15.29]	23.40 [17.62]	24.69 [17.82]	27.28 [20.64]
$\beta_{xyy}(-\omega; 0, \omega)$	17.34 [23.80]	21.31 [26.63]	5.46 [6.25]	6.59 [6.86]	6.36 [7.21]	7.72 [7.98]
$\beta_{xzz}(-\omega; 0, \omega)$	-0.18 [-0.03]	0.29 [-0.13]	0.25 [-0.06]	-0.05 [-0.13]	0.25 [-0.07]	-0.06 [-0.13]
$\beta_{xxx}(-2\omega; \omega, \omega)$	–	–	–	–	34.92 [25.66]	39.22 [30.13]
$\beta_{xyy}(-2\omega; \omega, \omega)$	–	–	–	–	9.69 [10.75]	11.90 [12.18]
$\beta_{xzz}(-2\omega; \omega, \omega)$	–	–	–	–	0.26 [-0.05]	-0.80 [-0.13]

Table 3
MP2/6-31G+p results for static linear polarizabilities (in 10^{-24} esu) and first hyperpolarizabilities (in 10^{-30} esu) of azo-enaminone isomers, and angles between the x -axis and the C_6-C_1 direction (in degree)

	1A_E [1A_Z]	1B_E [1B_Z]	1C_E [1C_Z]	2A_E [2A_Z]	3A_E [3A_Z]	4A_E [4A_Z]
$\alpha_{xx}(0;0)$	45.45 [40.66]	52.05 [44.16]	61.82 [50.34]	45.91 [42.08]	48.35 [44.46]	48.49 [45.08]
$\alpha_{yy}(0;0)$	34.44 [39.70]	35.77 [43.05]	39.43 [48.38]	36.28 [40.03]	32.18 [36.35]	35.15 [38.33]
$\alpha_{zz}(0;0)$	12.62 [12.68]	13.87 [13.90]	18.75 [18.64]	12.70 [12.72]	15.44 [15.12]	15.00 [15.05]
$\langle\alpha(0;0)\rangle$	30.84 [31.01]	33.90 [33.70]	40.00 [39.12]	31.63 [31.61]	31.99 [31.98]	32.88 [32.82]
$\beta_{xxx}(0;0,0)$	45.30 [24.58]	59.60 [23.22]	70.93 [21.01]	33.31 [18.84]	46.68 [29.59]	32.35 [18.70]
$\beta_{xyy}(0;0,0)$	21.31 [26.63]	22.64 [31.03]	22.24 [32.28]	19.14 [20.80]	5.70 [9.99]	7.36 [8.76]
$\beta_{xzz}(0;0,0)$	-0.29 [-0.13]	0.11 [0.01]	-0.06 [0.01]	-0.35 [-0.26]	0.47 [0.62]	0.26 [0.49]
$\beta_{vec}(0;0,0)$	66.32 [51.08]	82.35 [54.26]	93.11 [53.30]	52.10 [39.38]	52.85 [40.20]	39.97 [27.95]
Angle	7.3 [12.3]	6.5 [15.8]	4.8 [18.2]	12.9 [16.9]	4.0 [0.6]	2.5 [6.3]

increasing donor strength whereas the β_{xxx} values of the Z isomers decrease, indicating that the conjugated system of the E isomers provides a more effective interaction between donor and acceptor groups than that of the Z isomers. The $\mathbf{1B}_E/\mathbf{1A}_E$ [$\mathbf{1B}_Z/\mathbf{1A}_Z$] and $\mathbf{1C}_E/\mathbf{1B}_E$ [$\mathbf{1C}_Z/\mathbf{1B}_Z$] ratios show increases [decreases] of β_{xxx} by factors of 32% [5%] and 19% [10%], respectively. These results also indicate that to reach the saturation regime of this property would be required the incorporation of stronger donor groups [13]. The influence of the -OH group and/or Cl atom on the electric properties of the $\mathbf{1A}$ -type compounds can be estimated by comparisons with the results of the azo-enaminones **2**, **3** and **4**. One can see that the linear polarizability components are more sensitive to incorporation of a Cl atom at the phenyl ring (compounds **3** and **4**) than to the replacement of the H by OH (compounds **1A** and **2A**). Notice that the significant enhancement of α_{zz} is probably a consequence of the fact that the nitro group is rotated with respect to the plane of the phenyl ring with inclusion of the Cl atom. For the hyperpolarizability, it can be observed that the effects of incorporation of these substituents give a decrease of both β_{xxx} and β_{xyy} components. Therefore, the influence of Cl atom is particularly important for β_{xyy} which presents a marked reduction. For this component, the $\mathbf{3A}_E/\mathbf{1A}_E$ [$\mathbf{3A}_Z/\mathbf{1A}_Z$] and $\mathbf{4A}_E/\mathbf{1A}_E$ [$\mathbf{4A}_Z/\mathbf{1A}_Z$] ratios show decreases of 73% [62%] and 62% [58%], respectively.

Our results, in addition, show that the type of isomerization affect the components α_{xx} and α_{yy} but has effects almost negligible on α_{zz} . The MP2 ratios for $\mathbf{1A}_E/\mathbf{1A}_Z$, $\mathbf{1B}_E/\mathbf{1B}_Z$ and $\mathbf{1C}_E/\mathbf{1C}_Z$ show increases of 12%, 18% and

23% on α_{xx} and decreases of 13%, 17% and 18% on α_{yy} , respectively. A similar geometric effect on these components is also observed for the compounds **2**, **3** and **4**, although the corresponding increase (decrease) do not reach 10% (12%). One can see that the in-plane components α_{xx} and α_{yy} dominate the average linear polarizability of both isomers. In close analogy with effects of incorporation of stronger donor groups, the structural modifications have also a relevant impact for the diagonal component of the first hyperpolarizability. This means that the donor-acceptor intramolecular interaction in the direction of the dipole moment is also affected by the relative position of the π -conjugated system. For β_{xxx} the $\mathbf{1A}_E/\mathbf{1A}_Z$, $\mathbf{1B}_E/\mathbf{1B}_Z$ and $\mathbf{1C}_E/\mathbf{1C}_Z$ ratios indicate substantial increases by factors of 84%, 157% and 238%, respectively. A similar effect on the first hyperpolarizability components of tetra-substituted anthracene isomers with respect to relative position of the donor-acceptor groups have been recently reported [35]. It can be seen that for the E isomers the diagonal component β_{xxx} gives the main contribution to the magnitude of β_{vec} . Exception made for the compounds **3A_Z** and **4A_Z**, for the Z isomers the magnitude of β_{vec} has a similar contribution of both β_{xxx} and β_{xyy} components.

Dynamic results at the CPHF level for the first hyperpolarizability for two standard frequencies $\omega = 0.0239$ a.u. ($\lambda = 1907$ nm) and $\omega = 0.0428$ a.u. ($\lambda = 1064$ nm), obtained using MP2 optimized geometries, are reported in Table 4. The results show that for all molecules the dispersion effects increase as ω becomes large and have a major impact for the second harmonic generation than for electro-optical Pockels effect, as recently reported for

Table 4
CPHF/6-31G+p results for static and dynamic first hyperpolarizabilities (in 10^{-30} esu) of azo-enaminones isomers

Compound	Static	$\omega = 0.0239$		$\omega = 0.0482$	
	$\beta_{vec}(0;0,0)$	$\beta^K(-\omega;0,\omega)$	$\beta_{vec}(-2\omega;\omega,\omega)$	$\beta^K(-\omega;0,\omega)$	$\beta_{vec}(-2\omega;\omega,\omega)$
1A_E [1A_Z]	29.94 [24.38]	31.34 [25.50]	34.63 [28.25]	34.80 [28.37]	50.67 [41.81]
1B_E [1B_Z]	36.36 [25.85]	38.10 [27.11]	42.26 [30.15]	42.48 [30.26]	62.83 [45.44]
1C_E [1C_Z]	40.39 [25.94]	42.37 [27.21]	47.14 [30.33]	47.39 [30.42]	70.89 [46.10]
2A_E [2A_Z]	26.89 [20.54]	28.26 [21.61]	31.52 [24.21]	31.73 [24.33]	48.29 [37.88]
3A_E [3A_Z]	21.98 [16.23]	22.95 [16.96]	25.27 [18.77]	25.36 [18.80]	36.40 [27.52]
4A_E [4A_Z]	19.59 [12.65]	20.53 [13.25]	22.81 [14.75]	22.91 [14.75]	34.41 [22.30]

Table 5

HF/6-31G+p results for dipole moment (in D), static first hyperpolarizability (in 10^{-30} esu), first resonance frequency (in a.u.) and LUMO–HOMO energy gap (in a.u.) of azo-enaminones isomers

Compound	μ_x	β_{xxx}	ω_0	$\Delta E_{\text{LUMO-HOMO}}$
1A_E [1A_Z]	8.15 [7.70]	23.40 [17.62]	0.0710 [0.0703]	0.3144 [0.3154]
1B_E [1B_Z]	9.43 [8.68]	29.75 [16.38]	0.0709 [0.0685]	0.3098 [0.3103]
1C_E [1C_Z]	10.19 [9.14]	34.34 [15.12]	0.0706 [0.0679]	0.3084 [0.3090]

All calculations were performed using MP2/6-31G optimized geometry.

others organic systems [20,21,23]. Furthermore, for the EOPE effect, the dispersion correction leads to similar increases independent of the isomeric form and functional group added. The $\beta^{\text{K}}(-\omega; 0, \omega)$ values are augmented, with respect to static ones, by factors of the order of 5% and 17%, for $\omega = 0.0239$ a.u. and 0.0428 a.u., respectively. This is also true for SHG at $\omega = 0.0239$ a.u., where the corresponding augmentation is around 16%. At $\omega = 0.0428$ a.u., the dispersion effects are found to be larger (between 66% and 85%) and more dependent of the substituted isomer type because this frequency is comparable to the resonance frequency for $\beta_{\text{vec}}(-2\omega; \omega, \omega)$.

In Table 5 we present the first resonance frequencies of $\beta_{xxx}(-2\omega; \omega, \omega)$ for the **1**-type isomers together with the static μ_x and β_{xxx} values. All results listed in this table were calculated at HF/6-31G+p level using MP2 optimized geometry. One can observe, from these results, that the relative position of the absorption peak of $\beta_{xxx}(-2\omega; \omega, \omega)$ is slightly red shifted with the incorporation of donor groups with increasing strengths, regardless the isomeric form of the azo-enaminones. Similarly to observed for a series of alkyl derivatives of 4-amino- β -nitrostyrene [14] the energy shifts are consistent with the increase in μ_x . For the *E* isomers, where β_{xxx} gives a significant contribution to β_{vec} and β^{K} , one can see that these energy shifts are also consistent with the increase of this component. Additionally, the energies of the first electronic transition of the **1**-type isomers can be estimated as being twice of ω_0 quoted in Table 5. This transition energy represents the resonance frequency of $\beta_{xxx}(-\omega; 0, \omega)$ and for the compound **1A_E** [**1A_Z**], for instance, is estimated to be 0.1420 a.u. [0.1406 a.u.]. Regarding that the first transition can be estimated from the frontier molecular orbital energies, the energy gap between the lowest unoccupied molecular orbital (LUMO)

and the highest occupied molecular orbital (HOMO) are also quoted in Table 5. There is, therefore, a substantial discrepancy between the predictions of the first transition energies and the LUMO–HOMO energy gaps, indicating that for the azo-enaminone compounds the latter ones represent only a qualitative estimate of the first electronic transition.

In order to obtain a first estimation of the electron correlation effects on the first hyperpolarizability we have used the multiplicative correction scheme. It has been demonstrated that for donor–acceptor conjugated molecules the multiplicative approach provides a good estimate of the correlated frequency-dependent first hyperpolarizability [18]. The results for correlated dynamic first hyperpolarizability, together with the multiplicative scaling factors, are listed in Table 6. The scaling factors reveal that the electron correlation effects lead to substantial increases on the β_{vec} values. For the compound **1A_E** [**1A_Z**], in particular, the increase is of 122% [110%]. These results show the importance of electron correlation effects in theoretical studies specially if they are to be used for a rational design of new molecules with large quadratic NLO properties.

4. Conclusion

This study presents *ab initio* calculations of static and dynamic linear polarizabilities and first hyperpolarizabilities of donor–acceptor azo-enaminone isomers. Static and dynamic properties were determined at the CPHF level whereas correlated static properties were also calculated at the MP2 level. Two geometrical isomers have been considered in order to study effects of isomerization on the diagonal and off-diagonal components of the first hyperpolarizability. Our results show that the impact of the structural modifications for β_{xxx} is much more relevant than that observed for β_{xyy} . The diagonal component is strongly affected by the relative position of the π -conjugated system. For *E* isomers, the enhance of β_{xxx} for stronger donor groups is as consequence of the increase of the donor–acceptor intramolecular interaction in the direction of the dipole moment. The results also indicate that dispersion effects have a marked influence to second harmonic generation process at $\omega = 0.0428$ a.u. because this frequency is comparable to the resonance frequency for this process. In addition, comparisons between CPHF and MP2 results

Table 6

MP2/6-31G+p results for dynamic first hyperpolarizabilities (in 10^{-30} esu) of azo-enaminones isomers obtained using the multiplicative procedure

Compound	Scaling factor	$\omega = 0.0239$		$\omega = 0.0482$	
		$\beta^{\text{K}}(-\omega; 0, \omega)$	$\beta_{\text{vec}}(-2\omega; \omega, \omega)$	$\beta^{\text{K}}(-\omega; 0, \omega)$	$\beta_{\text{vec}}(-2\omega; \omega, \omega)$
1A_E [1A_Z]	2.22 [2.10]	69.57 [53.55]	77.88 [59.33]	77.26 [59.58]	112.49 [87.80]
1B_E [1B_Z]	2.26 [2.10]	86.11 [56.93]	95.51 [63.32]	96.01 [63.55]	141.99 [95.42]
1C_E [1C_Z]	2.31 [2.05]	97.87 [55.78]	108.89 [62.18]	109.47 [62.36]	163.76 [94.51]
2A_E [2A_Z]	1.94 [1.92]	54.82 [41.49]	61.15 [46.48]	61.56 [46.71]	93.68 [72.73]
3A_E [3A_Z]	2.40 [2.48]	55.08 [42.06]	60.65 [46.55]	60.86 [46.62]	87.36 [68.25]
4A_E [4A_Z]	2.04 [2.21]	41.88 [29.28]	46.53 [32.60]	46.74 [32.60]	72.20 [49.28]

obtained for static first hyperpolarizabilities demonstrate the importance of the incorporation of electron correlation effects in order to obtain accurate estimates of quadratic NLO properties.

Acknowledgements

The authors gratefully acknowledge the financial support of the CNPq, CAPES and FUNAPE/UFG Brazilian agencies.

References

- [1] S.R. Marder, D.N. Beratan, L.T. Cheng, *Science* 252 (1991) 103.
- [2] D.R. Kanis, M.A. Ratner, T.J. Marks, *Chem. Rev.* 94 (1994) 195.
- [3] F. Meyers, S.R. Mader, B.M. Pierce, J.L. Brédas, *J. Am. Chem. Soc.* 116 (1994) 10703.
- [4] S.R. Mader, B. Kippelen, A.K.Y. Jen, N. Peyghambarian, *Nature* 388 (1997) 845.
- [5] M.N. Eberlin, Y. Takahata, C. Kascheres, *J. Mol. Struct. (Theochem)* 207 (1990) 143.
- [6] P. Gilli, V. Bertolasi, V. Ferretti, G. Gilli, *J. Am. Chem. Soc.* 122 (2000) 10405.
- [7] B.L. Rodrigues, M.T.P. Gambardella, L. Figueiredo, C. Kascheres, *Acta Cryst.* C52 (1996) 705.
- [8] L.J.O. Figueiredo, C. Kascheres, *J. Org. Chem.* 62 (1997) 1164.
- [9] V. Macháček, A. Lyčka, Petr Šimůnek, T. Weidlich, *Magn. Reson. Chem.* 38 (2000) 293.
- [10] V. Kettmann, J. Lokaj, P. Šimůnek, V. Macháček, *Acta Cryst.* C57 (2001) 737.
- [11] P. Šimůnek, V. Bertolasi, V. Macháček, *J. Mol. Struct.* 642 (2002) 41.
- [12] I. Vencato, S. Cunha, V. Rocha, Z.N. da Rocha, C. Lariucci, *Acta Cryst.* E60 (2004) o1704.
- [13] T.L. Fonseca, H.C.B. de Oliveira, O.A.V. Amaral, M.A. Castro, *Chem. Phys. Lett.* 413 (2005) 356.
- [14] V. Keshari, S.P. Karna, N. Prasad, *J. Phys. Chem.* 97 (1993) 3525.
- [15] H. Sekino, R.J. Bartlett, *Chem. Phys. Lett.* 234 (1995) 87.
- [16] F. Aiga, R. Itoh, *Chem. Phys. Lett.* 251 (1996) 372.
- [17] E.K. Dalskov, H.J.Aa. Jensen, J. Oddershede, *Mol. Phys.* 90 (1997) 3.
- [18] D. Jacquemin, B. Champagne, C. Häting, *Chem. Phys. Lett.* 319 (2000) 327.
- [19] D. Jacquemin, B. Champagne, E.A. Perpète, J.M. Luis, B. Kirtman, *J. Phys. Chem. A* 105 (2001) 9748.
- [20] W. Zhu, G.-S. Wu, *Chem. Phys. Lett.* 358 (2002) 1.
- [21] D. Jacquemin, E.A. Perpète, J.M. André, *J. Chem. Phys.* 120 (2004) 10317.
- [22] D. Jacquemin, O. Quinet, B. Champagne, J.M. André, *J. Chem. Phys.* 120 (2004) 9401.
- [23] A. Alparone, A. Millefiori, S. Millefiori, *Chem. Phys. Lett.* 409 (2005) 288.
- [24] B. Champagne, B. Kirtman, *J. Chem. Phys.* 125 (2006) 024101.
- [25] B. Champagne, *Chem. Phys. Lett.* 261 (1996) 57.
- [26] H.C.B. de Oliveira, T.L. Fonseca, M.A. Castro, O.A.V. Amaral, S. Cunha, *J. Chem. Phys.* 119 (2003) 8417.
- [27] M.J. Frisch et al., *GAUSSIAN 03, Revision C.02*, Gaussian, Inc., Pittsburgh, PA, 2004.
- [28] D.M. Bishop, *Adv. Chem. Phys.* 104 (1998) 1.
- [29] B.F. Levine, C.G. Bethea, *Appl. Phys. Lett.* 24 (1974) 445.
- [30] S.J. Lalama, A.F. Garito, *Phys. Rev. A* 20 (1979) 1179.
- [31] K. Clays, A. Persoons, *Phys. Rev. Lett.* 66 (1991) 2980.
- [32] T. Tsunekawa, K. Yamaguchi, *J. Phys. Chem.* 96 (1992) 10268.
- [33] K.O. Sylvester-Hvid, P.O. Åstrand, M.A. Ratner, K.V. Mikkelsen, *J. Phys. Chem. A* 103 (1999) 1818.
- [34] M. Yang, S. Li, J. Ma, Y. Jiang, *Chem. Phys. Lett.* 354 (2002) 316.
- [35] M. Tomonari, N. Ookubo, *Chem. Phys. Lett.* 376 (2003) 504.