Theoretical study of the static first hyperpolarizability of azo-enaminone compounds

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In this work the static electric properties of azo-enaminones, with special emphasis to the vector component of the first hyperpolarizability β_{vec}, are determined at the Hartree–Fock (HF) level with the electron correlation (EC) effects included through the second-order Møller–Plesset perturbation theory (MP2). The *ab initio* results, in accordance with previous semiempirical calculations, show that appropriate choices of substituents to be incorporated to the molecular structure can have a marked influence on the first hyperpolarizability. An initial study about the changes on the β_{vec} values of these compounds, as a result of the incorporation of different donor groups, indicates that this property increases as function of the donor group strength tending to a saturated value. A comparison between our HF and MP2 results, for all compounds studied here, show that the β_{vec} values are strongly affected by the effects of the electron correlation correction. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1612474]

I. INTRODUCTION

Organic materials that exhibit large nonlinear optical (NLO) properties have emerged as an important class of electronic materials with interesting characteristics for photonic applications.[1–3] In the last decade, based on the two level model,[4,5] several experimental studies have focused attention on the question of the understanding and design of new chromophores with large quadratic NLO properties.[6–12] Marder *et al.*[11,12] have showed, for example, that the strength of electron donor and acceptor groups, connected to an organic π-delocalized framework, should be optimized in order to maximize the first hyperpolarizability. Besides, the experimental flexibility of chemical manipulations in the synthesis of new organic molecules is a fundamental step in the advance of photonic technology, since new structures can be synthesized with desired characteristics for specific applications. Then, an important feature in the search and optimization of new NLO molecules is the understanding of the process by which chemical substitutions affects their first hyperpolarizability. On the theoretical side, quantum chemical calculations may also play a crucial role in the design of new NLO chromophores as they may provide some guidance for rational choices of molecular synthesis of new organic molecules.

Enaminones are chemical substances that present a conjugated system of the type N–C═C–C═O with different geometric forms.[13,14] Such compounds are extremely valuable synthetic intermediates with interesting properties that can be used as agents in preparation of antibacterial[15] and anticonvulsant[16] drugs. Nowadays, pharmacological applications involving these compounds constitute the object of growing interest of research.[14,16,17] A particular class of enaminones are the azo-enaminones which are obtained by incorporation of an azo group to the N–C═C–C═O con-

jugated system.[18–22] The presence of the azo group plays an important role on the optical activities of the system. Besides, these azo-enaminone compounds have a planar molecular architecture favored by the intramolecular hydrogen bonds involving the azo group.[18,19] The first theoretical study concerning the NLO properties of azo-enaminones derivatives was performed by Figueiredo and Kascheres, using the AM1 semiemprirical method.[19] Based on these calculations, they have proposed such compounds as candidates for second-order NLO applications.

The NLO molecules studied in this work are displayed in Fig. 1 and Table I. The NLO molecules **1** and **2** were synthesized from the azo coupling between quinone diazides and acyclic enaminones.[18,19] Compounds **3** and **4** can be obtained through the coupling of diazonium salts and enaminones. In particular, compounds **4** were obtained by one of us. Macháček *et al.*[20,22] have also synthesized molecules with a similar chemical structure. In this work, we present an *ab initio* investigation of the nonlinear optical properties of these new azo-enaminones with appropriate substituents as well as some azo-enaminones studied by Figueiredo and Kascheres.[19] For the azo-enaminones with electron acceptor group (such as the nitro group) attached at *para* position of the phenyl ring, our systematic *ab initio* investigation is based on the replacement of H of the aminic group by substituents with increasingly donor strength such as $-CH_3$ and $-C(CH_3)_3$. The dipole moment, linear polarizability and first hyperpolarizability were calculated at HF and MP2 levels using the analytical (AN) and finite field (FF) approaches. MP2 calculations have demonstrated the importance of inclusion of the electron correlation effect in order to obtain accurate estimates for the linear and nonlinear polarizabilities for different organic systems.[23–29] Good agreement between theoretical and experimental results for NLO proper-
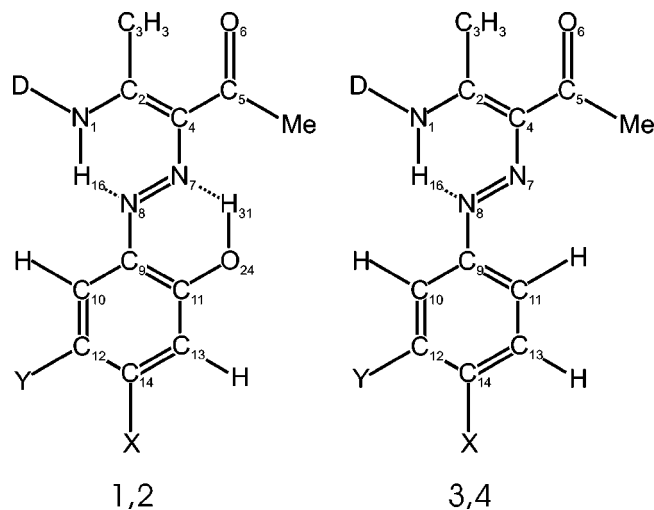
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FIG. 1. Molecular structures of the azo-enaminones studied in this work (see also Table I).

ties of small molecules through accurate *ab initio* calculations including electron correlation effects, have also been reported.[30,31]

II. COMPUTATIONAL DETAILS

In presence of a static uniform electric field (F) the perturbed energy (E) of a molecule can be written as

$$E(F) = E_0 - \sum_i \mu_i F_i - \frac{1}{2!} \sum_{ij} \alpha_{ij} F_i F_j$$
$$- \frac{1}{3!} \sum_{ijk} \beta_{ijk} F_i F_j F_k - \cdots, \tag{1}$$

where E_0 is the energy of the molecule in the absence of an external electric field and μ_i are the components of the permanent dipole moment; α_{ii} are the components of the dipole polarizability; and β_{ijk} are the components of the first dipole hyperpolarizability. Here the average linear polarizability

TABLE I. Labels of the azo-enaminones presented in Fig. 1.

		Substituents	
Compounds	D	X	Y
1A	H	H	Cl
1B	H	NO$_2$	Cl
1C	Me	NO$_2$	Cl
1D	t-Bu	NO$_2$	Cl
2A	H	H	H
2B	H	NO$_2$	H
2C	Me	NO$_2$	H
2D	t-Bu	NO$_2$	H
3A	H	H	Cl
3B	H	NO$_2$	Cl
3C	Me	NO$_2$	Cl
3D	t-Bu	NO$_2$	Cl
4A	H	H	H
4B	H	NO$_2$	H
4C	Me	NO$_2$	H
4D	t-Bu	NO$_2$	H

$\langle \alpha \rangle$ and the vector component of the first hypepolarizability along the dipole moment direction β_{vec} (Refs. 2, 7) are defined by the following equations:

$$\langle \alpha \rangle = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \tag{2}$$

and

$$\beta_{vec} = \sum_i \beta_i \mu_i / |\mu| \quad [i = x, y, z], \tag{3}$$

where μ is the ground-state dipole moment and with β_i given by

$$\beta_i = \sum_k \beta_{ikk} \quad [i, k = x, y, z]. \tag{4}$$

The component β_{vec} defined above is the quantity measured in electric field induced second harmonic generation (EFISH) experiments.[32–34] It should be stressed that experimental β_{vec} is frequency dependent while in this work only static values are reported. Another quantity of interest is the total intrinsic quadratic hyperpolarizability given by

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}. \tag{5}$$

Note that

$$\beta_{vec} / \beta_{tot} = \cos \theta, \tag{6}$$

where θ is the angle between the vector formed by the β_i components and the dipole moment vector.

In *ab initio* polarizability calculations of small molecules the inclusion of the electron correlation effects may be accomplished by a sequence of increasingly sophisticated theoretical methods.[30,31] For large organic molecules however, giving the computational difficulties involved, the treatment of the electron correlation is usually restricted to the MP2 level. Considering that the MP2 method normally provides a major contribution to the total EC effects it has been used as the starting point in the discussion of the EC role in calculations involving these molecules.[24,28] Based on MP2 calculations, Sim *et al.*[23] reported that the inclusion of EC effects leads to a remarkable increase on the β values for *P*-nitroaniline (PNA). More recently, Yang *et al.*[27] showed that the longitudinal component of the second hyperpolarizability (γ) of centrosymmetric squaraines is very sensitive to EC effects.

Here HF dipole moment and polarizabilities were calculated analytically using the coupled perturbed Hartree–Fock (CPHF) procedure. At the MP2 level, the calculation of these properties were performed numerically using the finite field method. Within FF numerical approach, the appropriate choice of electric field strengths play a crucial role in the numerical stability of the results as showed by Sim *et al.*[23] in the calculation of the first hyperpolarizabilities of PNA. For all azo-enaminone compounds, the MP2 properties were obtained from FF calculations using positive and negative field strengths in the range of 0.001 a.u. The validity of FF numerical procedure employed here was examined at HF level. For a representative set of azo-enaminones, this examination showed that the numerical and analytical procedures leads to equivalent results for the dipole moment and polarizabilities.

TABLE II. HF and MP2 optimized bond distance (in Å) values for azo-enaminones **4B** and **1B′** computed with different basis sets.

| | **4B** | | | | **1B′** | | |
| | HF | | MP2 | | HF | MP2 | |
	6-31G	6-31G*	6-31G	6-31G*	6-31G	6-31G	Expt.[a]
$d(N_1C_2)$	1.326	1.320	1.353	1.333	1.329	1.355	1.314
$d(C_2C_3)$	1.505	1.508	1.519	1.501	1.505	1.519	1.493
$d(C_2C_4)$	1.405	1.404	1.422	1.414	1.393	1.412	1.422
$d(C_4C_5)$	1.465	1.476	1.489	1.482	1.458	1.483	1.451
$d(C_5O_6)$	1.233	1.205	1.274	1.238	1.225	1.259	1.220
$d(C_4N_7)$	1.374	1.375	1.401	1.375	1.372	1.393	1.365
$d(N_7N_8)$	1.252	1.237	1.326	1.298	1.247	1.333	1.300
$d(N_8C_9)$	1.416	1.415	1.443	1.417	1.416	1.433	1.412
$d(C_9C_{10})$	1.395	1.395	1.417	1.405	1.401	1.435	1.392
$d(C_9C_{11})$	1.392	1.390	1.414	1.402	1.390	1.416	1.385
$d(C_{10}C_{12})$	1.380	1.378	1.407	1.390	1.386	1.413	1.392
$d(C_{11}C_{13})$	1.381	1.381	1.408	1.392	1.374	1.398	1.382
$d(C_{12}C_{14})$	1.387	1.386	1.409	1.396	1.379	1.402	1.380
$d(C_{13}C_{14})$	1.385	1.382	1.406	1.392	1.388	1.412	1.387
$d(C_{14}N_{15})$	1.444	1.454	1.489	1.468	1.450	1.473	1.484

[a]Results obtained from Ref. 18.

The electric properties and geometry optimization calculations, at HF and MP2 levels, were performed using the GAUSSIAN 98[35] electronic structure package.

It is also worthwhile stressing that in *ab initio* calculations the choice of basis set is an as important ingredient as the inclusion of electron correlation effects. The most commonly used basis set in calculations involving large organic molecules is the split valence 6-31G basis set.[24,25] Theoretical studies have showed however, that this set supplemented by the addition of diffuse p and d functions, provides a considerable improvement on the estimates of the second hyperpolarizability of small organic molecular systems.[26,27,29,36,37] Tsunekawa and Yamaguchi[38] concluded that for donor-acceptor nitrogen-containing molecules the 6-31G basis set plus one additional diffuse p or d functions on the carbon and nitrogen atoms leads to qualitative improvements on the β values. It is also our purpose in this work to study the basis set effects on the polarizabilities of azo-enaminones by comparing the results obtained using the 6-31G basis set and two augmented versions of this set, namely, the 6-31G+p and 6-31G+d basis sets (extra p and d functions are added on the heavy atoms). Following Tsunekawa and Yamaguchi,[38] the choice of the exponents of the p or d functions on each heavy atom was determined, at the HF level, by imposing the maximization of the β_{vec} value. This criterion is justifiable because the use of relatively small basis sets tends to underestimate the values of the calculated properties.

III. RESULTS AND DISCUSSION

Table II shows optimized bond distances for molecule **4B** obtained with the 6-31G and 6-31G* basis sets at HF and MP2 levels. The calculated values at HF and MP2 levels for the azo-enaminone **1B′** (molecule obtained from **1B** by substitution of −CH$_3$ by −OCH$_2$CH$_3$) using the 6-31G basis set are also included together with the experimental values determined by x-ray diffraction.[18] The results obtained indicate that the bond distances are only slightly modified after

reoptimization using the 6-31G* basis set. As observed for other organic systems,[27,29] the electron correlation effects increase the optimized bond distances in comparison with the corresponding HF values. Nevertheless, one can observe that there is a good agreement between our HF/6-31G and MP2/6-31G results and these experimental data, indicating that the HF/6-31G calculations can provide good estimates of the molecular geometry of these compounds. A similar conclusion have been drawn by Abe *et al.*[39] for heterocyclic pyridinium betaines. Despite the small differences between the optimized bond lengths at HF and MP2 levels of calculations, the geometry of each azo-enaminone compound was fully optimized at both levels using the 6-31G basis set. Our *ab initio* calculations have also shown that all optimized structures are planar.

Comparisons with pure single and double bond results obtained from the literature for N=C=1.27 Å,[21,40] C−C =1.49 Å,[21,41] C−N=1.45 Å,[21,40] N−N=1.41 Å,[21,40] N=N=1.23 Å,[21,39] show that the bond distances calculated here have intermediate values between these single and double bonds. For instance, MP2 (HF) bond distance values obtained with 6-31G basis set for the central part of compound **4B** are: N$_1$−C$_2$=1.353 Å (1.326Å), C$_2$−C$_4$ =1.422 Å (1.405 Å), C$_4$−N$_7$=1.401 Å (1.374 Å), N$_7$−N$_8$ =1.326 Å (1.252 Å). These results confirm the existence of an extensive conjugation throughout the molecule leading to an increase of the mobility of the π-electrons which in turn can have a beneficial effect on the increase of the first hyperpolarizability. Results obtained, but not listed here, show that even the incorporation of strong donor groups at the aminic nitrogen (N$_1$) (such as in compounds **C** and **D**) practically does not affect the geometry of these compounds. In azo-enaminones with a chlorine atom and a nitro group attached at the phenyl ring (such as in compounds **1B**, **1C**, **1D**, **3B**, **3C**, and **3D**) the spatial interaction leads to a rotation of the nitro group. For these compounds, the MP2/6-31G and HF/6-31G dihedral angles between the nitro group and the

TABLE III. HF and MP2 optimized hydrogen bond parameters for azo-enaminones **4B** and **1B**′ computed with different basis sets. The bonds are in Å and angles in degree.

| | **4B** | | | | **1B**′ | | |
| | HF | | MP2 | | HF | MP2 | |
	6-31G	6-31G*	6-31G	6-31G*	6-31G	6-31G	Expt.[a]
$d(N_1H_{16})$	1.000	0.999	1.031	1.030	0.998	1.028	0.940
$d(N_8H_{16})$	1.885	1.922	1.794	1.776	1.951	1.854	1.917
$d(N_1N_8)$	2.626	2.639	2.602	2.579	2.679	2.648	2.584
$\angle N_1H_{16}N_8$	128.40	126.26	132.27	131.53	127.57	131.38	126.00
$d(N_7H_{31})$	-	-	-	-	1.942	1.782	1.887
$d(H_{31}O_{24})$	-	-	-	-	0.962	1.008	0.920
$d(N_7O_{24})$	-	-	-	-	2.647	2.611	2.568
$\angle N_7H_{31}O_{24}$	-	-	-	-	128.32	137.07	129.00

[a]Results obtained from Ref. 18.

phenyl ring have values around 50° and 36°, respectively. Such values are not affected by incorporation of the donor groups.

In accordance with previous x-ray structural determination[18] and AM1 results,[19] both HF and MP2 optimized geometries show that the azo-enaminones **1** and **2** have two intramolecular hydrogen bonds. This is expected because the molecules are planar and the OH is *cis* to C_9-C_{11}. The MP2 and HF hydrogen bond parameters for the compounds **4B** and **1B**′, including the corresponding experimental values, are presented in Table III. Note that comparisons between the hydrogen bond parameters of compound **1B**′ with the corresponding experimental data show discrepancies in the range of 0.1 Å. In contrast with the results for compounds **1** and **2**, the central part of azo-enaminones **3** and **4** have just one intramolecular hydrogen bond. For these compounds, planarity is favored by the intramolecular hydrogen bond.

Table IV shows HF and MP2 results for the dipole moment, linear polarizability and first hyperpolarizability of azo-enaminones **4**, obtained using the 6-31G, 6-31G+p and 6-31G+d basis sets. The exponents that maximizes the β_{vec} values when p and d extra functions are added on heavy atoms are: $\zeta_p=0.03$ and $\zeta_d=0.03$ on carbon atoms, $\zeta_p=0.04$ and $\zeta_d=0.09$ on nitrogen atoms, $\zeta_p=0.07$ and $\zeta_d=0.09$ on the oxygen atom. For the compounds **1** and **3**, the

exponent of p extra function on chlorine atom is $\zeta_p=0.02$. Basically, the addition of a diffuse function leads to a systematic increase on each calculated property, at the HF and MP2 levels. As can be seen the addition of p diffuse functions has almost no impact on the μ estimates and only a minor effect on the linear polarizability (an increase in the range of 10%). Our results for the first hyperpolarizability reveal a slightly larger dependence on the basis set. The use of the 6-31G+p basis set increases the β_{vec} values, as compared with those obtained with the 6-31G basis set, by an amount which varies between 11% to 22%. HF results for compounds **A** constitute exceptions to this behavior probably as a consequence of the small magnitude of β_{vec} for these compounds. It can be noticed that the 6-31G+p basis set gives results that are almost identical to those obtained using the 6-31G+d basis set, indicating that the addition of one p or one d diffuse function have an equivalent impact on the improvement of the calculated properties for these NLO molecules. A similar conclusion, with respect to basis set effects, for donor–acceptor nitrogen-containing molecules, was reported by Tsunekawa and Yamaguchi.[38]

In order to assess the importance of the EC effects on the calculation of these properties one can start with a first estimate, obtained using the HF equilibrium geometry as the fixed geometry in a MP2 calculation. This contribution has

TABLE IV. HF and MP2 dipole moment (in D), linear polarizability (in 10^{-24} esu) and first hyperpolarizability (in 10^{-30} esu) values for compounds **4** computed using different basis sets.

| | μ | | | $\langle\alpha\rangle$ | | | β_{vec} | | |
	6-31G	6-31G+p	6-31G+d	6-31G	6-31G+p	6-31G+d	6-31G	6-31G+p	6-31G+d
HF level									
4A	3.97	4.03	4.00	20.58	22.69	22.96	0.13	−0.62	−0.19
4B	7.20	7.29	7.16	23.85	26.04	26.59	17.75	19.80	19.04
4C	8.11	8.30	8.13	25.86	28.05	28.62	18.36	21.32	20.12
4D	8.68	8.87	8.77	30.48	32.89	33.45	18.42	21.29	20.58
MP2 level									
4A	3.96	4.09	4.02	23.18	26.18	26.45	−3.13	−4.23	−3.69
4B	5.95	6.22	6.09	27.61	31.01	31.60	43.39	51.12	49.46
4C	7.00	7.14	7.31	30.27	33.71	34.33	44.54	54.15	51.19
4D	7.49	7.94	7.90	35.29	39.13	39.71	43.80	53.29	51.51

TABLE V. HF and MP2 μ (in D) values for azo-enaminones computed using different basis sets.

Compounds	HF		MP2		
	6-31G	6-31+p	6-31G[a]	6-31G	6-31+p
1A	3.03	3.34	3.43	3.79	3.87
1B	8.80	8.84	7.67	8.07	8.28
1C	9.60	9.72	8.55	9.02	9.41
1D	10.15	10.30	9.10	9.53	9.95
2A	5.20	5.25	4.79	5.06	5.23
2B	8.62	8.70	7.46	7.87	8.17
2C	9.46	9.63	8.38	8.87	9.35
2D	10.04	10.25	8.95	9.40	9.91
3A	1.63	1.66	1.99	1.95	2.02
3B	7.59	7.60	6.23	6.15	6.32
3C	8.40	8.49	7.16	7.09	7.42
3D	8.93	9.06	7.72	7.55	7.90
4A	3.97	4.03	3.94	3.96	4.09
4B	7.20	7.29	5.95	5.95	6.22
4C	8.11	8.30	6.97	7.00	7.14
4D	8.68	8.87	7.54	7.49	7.94
PNA	8.21	8.54	7.06	7.05	7.35

[a]Results obtained with HF geometry.

TABLE VI. HF and MP2 $\langle \alpha \rangle$ (in 10^{-24} esu) values for azo-enaminones computed using different basis sets.

Compounds	HF		MP2		
	6-31G	6-31+p	6-31G[a]	6-31G	6-31+p
1A	22.80	24.78	24.17	26.12	29.06
1B	25.63	27.81	27.21	29.43	32.80
1C	27.68	29.84	29.65	32.02	35.37
1D	32.24	34.63	34.46	36.93	40.66
2A	21.11	23.18	22.35	24.17	27.19
2B	24.23	26.39	25.70	28.18	31.58
2C	26.31	28.45	28.19	30.92	34.34
2D	30.92	33.28	33.06	35.93	39.72
3A	22.21	24.25	23.40	25.04	27.99
3B	25.21	27.44	26.86	28.59	31.95
3C	27.28	29.49	29.38	31.24	34.62
3D	31.86	34.30	34.23	36.18	39.99
4A	20.58	22.69	21.66	23.18	26.18
4B	23.85	26.04	25.46	27.61	31.01
4C	25.86	28.05	27.88	30.27	33.71
4D	30.48	32.89	32.78	35.29	39.13
PNA	11.28	13.49	11.89	12.64	14.83

[a]Results obtained with HF geometry.

been defined as the direct effect of the electron correlation[25] which is mostly related to changes in the electronic structure. Another part of the EC effect, which is mainly related to shifts in the equilibrium geometry, is obtained using the MP2 optimized equilibrium geometry in a MP2 calculation. This is defined as the indirect effect of electron correlation. The overall EC effect is given as a combination of both, direct and indirect, effects. Tables V–VII show the HF and MP2 results obtained using the 6-31G and 6-31G+p basis sets for the dipole moment, linear polarizability and first hyperpolarizability for the azo-enaminones 1, 2, 3, and 4. We have also included, for the sake of comparison, the optical properties of PNA. In this section the discussion will be focused on the 6-31G results. Comparison with the HF results displayed in Table V show that exception made to the compounds 1A and 3A, for all other compounds the direct EC effects diminishes the μ values by at most 18%. In particular, for chromophores 4B, 4C, and 4D, the factors of reduction obtained by MP2// HF/HF//HF ratios are, respectively, 17%, 14% and 13%. The indirect effect on μ, given by MP2//MP2/MP2//HF, is less important: reaching +6% for compounds 1 and 2 and being neglegiable for compounds 3 and 4. The inclusion of EC leads to systematic increases on the $\langle \alpha \rangle$ values (see Table VI). Each effect, direct and indirect, increase the calculated values by an amount which varies between 5 and 10%. The results presented in Table VII show that the contribution of the EC effects to the first hyperpolarizability is much more important than that observed for the linear polarizability. For these compounds, a remarkable increase on the correlated β_{vec} values arises from the changes in the electronic structure. Exception made to compounds 1A, 2A, and 4A, the direct EC effect gives rise to an increase which varies between 70 and 100%. For compounds 2 and 4, which do not include the Cl atom, the indirect EC effect also increases the β_{vec} values by an amount around 30%. For compounds 1 and 3, which contain the Cl atom, the indirect EC effect is less important leading in some cases to a diminution of the

β_{vec} values. In particular, for compounds 4B, 4C, and 4D the overall EC effect increases the β_{vec} values by factors of, respectively, 144%, 143% and 138%. These figures leave no doubt about the importance of EC effects in theoretical studies specially if these results is meant to provide indications for molecular synthesis of new NLO molecules.

In order to analyze the changes on the optical properties of these azo-enaminone compounds as a result of the incorporation of the nitro group and other strong donor groups, we focus our attention on the 6-31G+p results. One can observe from Table VI that the introduction of substituents lifts the linear polarizability values. The $\langle \alpha \rangle$ results, at the HF and MP2 levels, for the sequence A, B, C, and D, show a systematic increase which is consistent with the incorpora-

TABLE VII. HF and MP2 β_{vec} values (in 10^{-30} esu) for azo-enaminones computed using different basis sets.

Compounds	HF		MP2		
	6-31G	6-31+p	6-31G[a]	6-31G	6-31+p
1A	2.03	2.49	5.47	5.49	5.49
1B	12.75	13.76	22.94	24.99	27.86
1C	13.46	15.22	23.93	22.83	27.01
1D	13.36	14.94	23.34	20.67	24.45
2A	−0.43	−1.33	0.86	−0.06	−1.07
2B	14.29	15.49	24.29	33.21	38.65
2C	15.07	17.15	25.93	34.31	41.69
2D	14.97	16.89	25.68	33.10	40.28
3A	3.08	3.80	5.99	6.82	5.94
3B	16.69	18.23	33.46	35.90	40.11
3C	17.67	20.06	35.14	34.70	40.32
3D	17.84	20.08	34.76	32.82	38.12
4A	0.13	−0.62	−0.97	−3.13	−4.23
4B	17.75	19.80	32.52	43.39	51.12
4C	18.36	21.32	34.15	44.54	54.15
4D	18.42	21.29	34.23	43.80	53.29
PNA	9.01	12.24	16.22	20.24	25.15

[a]Results obtained with HF geometry.

tion of each one of the different substituents. Yang *et al.*[27] have observed a similar trend for the α values of centrosymmetric squaraines. Looking at Table V one can see that the MP2 (HF) **4B/4A** ratios show that the incorporation of the nitro group increases the μ values by 52% (81%), while for **4C/4B** and for **4D/4C** ratios the increase are, respectively, of the order of 15% (14%) and 11% (7%). Since the compounds **A** have no nitro group attached at the phenyl ring, they present the smallest results for μ. As regards the results for β_{vec} (see Table VII), it is worthwhile noticing that a previous study[19] have shown that *p*-nitro azo-enaminones possess much larger β_{vec} values than the corresponding values for the compounds **A**. Confirming this finding, our results for β_{vec} obtained at the HF level changes from -0.62 esu for **4A** to 19.80 esu for **4B** while at the MP2 level the corresponding change goes from -4.23 to 51.12 esu. The MP2 (HF) ratios for **4C/4B** reveal an increase of 6% (8%) while those for **4D/4C** are practically equal to one. These results show that within the family of compounds **4** the evolution of the β_{vec} ratio, as function of the incorporation of stronger donor groups, indicates a clear saturation trend. A similar conclusion is also verified for molecules **1**, **2** and **3**. This behavior is also observed for donor–acceptor polyene systems, for which experimental measures have shown that the incorporation of increasingly stronger acceptors does not necessarily increase the first hyperpolarizability.[12]

We have also investigated the substitution effects of the nitro group at the *ortho* and *meta* positions on the first hyperpolarizability of azo-enaminone **4B**. Our MP2/6-31G β_{vec} (β_{tot}) results for the *p*-nitro, the *o*-nitro and the *m*-nitro azo-enaminone are, respectively, 43.39×10^{-30} (58.60×10^{-30}) esu, 5.72×10^{-30} (27.66×10^{-30}) esu and 20.75×10^{-30} (31.66×10^{-30}) esu. These results show that both *o*-nitro and *m*-nitro substitutions changes the electron-withdrawing ability of the nitro group, leading to a marked diminution of the β_{vec} values. Note that these substitutions decrease of the β_{tot} values and, at the same time, increase the θ angle. It should be stressed that for the *o*-nitro azo-enaminone the angle between the vector formed by the β_i components and the dipole moment vector is 78°, which is very large as compared with the angles for the *p*- and *m*-nitro azo-enaminones.

Our results show, in addition, that different functional groups bonded to phenyl ring does not have a beneficial effect on the first hyperpolarizability. The influence of a chlorine atom or an OH group on the properties of the **4**-type compounds can be estimated, respectively, by comparisons between the results for the azo-enaminones **3** and **4** and between the azo-enaminones **2** and **4**. As can be seen from Table VI, the difference between the $\langle \alpha \rangle$ values for molecules **2B**, **3B**, and **4B** does not reach 6%. In contrast, the presence of these substitutions has a marked effect on the first hyperpolarizability. Excluding the compounds **A**, which do not have a nitro group attached, our MP2 (HF) results for the **3B/4B**, **3C/4C**, and **3D/4D** ratios show that the β_{vec} values diminish with the inclusion of the Cl atom by factors of, respectively, 22% (8%), 26% (6%) and 28% (6%). It should be remembered as stated before, that in compounds with a chlorine atom, the nitro group attached at phenyl ring

is rotated. Although the planarity of the molecule as a whole is not perturbed, this spatial interaction reduce the charge transfer between the donor group and the nitro group leading, consequently, to the observed decrease on the β_{vec} values of the compounds **3**. It should also be noted that the absence of a Cl atom have only a minor impact on the μ values for compounds **B**, **C**, and **D**.

As regards the presence of the OH group bonded at the phenyl ring our results show a reduction of the push-pull intensity throughout the backbone of the molecules, which results in a diminution of the β_{vec} values of compounds **2** in comparison with the results for compounds **4**. For instance, MP2 and (HF) **2B/4B**, **2C/4C**, and **2D/4D** ratios show that the β_{vec} decrease with the inclusion of the OH group, respectively, by 24% (22%), 23% (20%) and 24% (21%). Differently, the inclusion of this group increase the dipole moment values by factors of, respectively, 31% (19%), 31% (16%) and 25% (16%). These latter results lead to the conclusion that the dipole–dipole electrostatic interaction is weaker for the compounds **4**, an aspect that should be taken into account in the design of macroscopic structures with NLO optical properties.[42]

IV. CONCLUSION

In this paper the dipole moment, linear polarizability and first hyperpolarizability of azo-enaminones are systematically investigated at the HF and MP2 levels. Special emphasis is given to the calculation and analysis of the first hyperpolarizability. As expected, inclusion of electron correlation effects plays a major role on the calculation of the β_{vec}. The calculated results for the *p*-nitro azo-enaminones studied here show that enhanced β_{vec} values can be obtained by appropriate choices of the substituents. Our results also indicate that the incorporation of increasing donor strength groups leads to a saturation of β_{vec}. They also show that a Cl atom and OH group attached at the phenyl ring reduces the push-pull intensity throughout the molecule, decreasing the first hyperpolarizability. On the experimental side, the **4**-type compounds, synthesized by coupling of diazonium salts, are more flexible with respect to desired structural modifications than the **1**, **2**-type compounds, which are synthesized by quinone diazide route. Considering this feature and the enhanced β_{vec} values estimated in this work, it is our belief that the **4**-type compounds studied here may open new possibilities in the design process of new NLO chromophores based on azo-enaminone compounds for use in applications of nonlinear optics.

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