J. Phys. Chem. A **1997,** *101,* 3025−3031

An ab Initio and Semiempirical Study of the First- and Third-Order Polarizabilities in Benzene and Thiophene Derivatives: Electron Correlation Effects

C. Adant,[†] J. L. Brédas,*,[†] and M. Dupuis[‡]

Service de Chimie des Matériaux Nouveaux, Centre de Recherche en Electronique et Photonique Moléculaires, Université de Mons-Hainaut, Place du Parc 20, B-7000 Mons, Belgium, and Pacific Northwest Laboratory, EMLS/K1-90, Battelle Boulevard, Richland, Washington 99352

Received: October 1, 1996; In Final Form: February 14, 1997[⊗]

The static first- and third-order polarizabilities of several benzene and thiophene derivatives are evaluated at the ab initio level via an efficacious general finite field approach. The impact of electron correlation is explored by calculating the molecular polarizabilities at the Møller−Plesset second-order perturbation (MP2) theory level using an extended basis set. Further, we examine the influence of molecular architecture on the nonlinear optical response, in particular the switch from an arylethenyl type of structure to a quinoid structure. Finally, we apply the correction vector method combined with the intermediate neglect of differential overlap−single and double excitation configuration interaction (INDO-SDCI) technique to evaluate the optical nonlinearities at the semiempirical level. The reliability of this procedure is established by comparison with the corresponding high-level ab initio polarizability values. The results clearly show the sensitive dependence of the nonlinear optical properties on electron correlation effects that are found to quantitatively and qualitatively affect the third-order polarizability values.

Introduction

Conjugated organic compounds exhibiting a high nonlinear optical response have attracted considerable attention, as is exemplified by numerous recent experimental and theoretical investigations.[1−7] The ease with which these materials can be chemically modified and their properties tuned makes them ideal candidates for optoelectronic and photonic applications. The key to design novel suitable nonlinear optical (NLO) organic materials and/or to modify known compounds lies in the complete determination of the structure−molecular polarizabilities relationships; quantum chemistry methods can thus be particularly helpful in this context.

The attention devoted to the evaluation of the third-order nonlinear optical response of π-conjugated oligomeric and polymeric systems[2,3,6] has resulted in a vast amount of theoretical studies, performed at the ab initio[8−13] or semiempirical[14−19] levels on various classes of conjugated organic compounds. Despite intensive investigations, the evaluation of the third-order polarizability γ in large molecules is still an ongoing problem. At the present time, quantitative estimates of third-order polarizabilities can only be performed on small systems. Even if one is merely interested in establishing trends in the nonlinear optical properties among a series of structurally related molecules, the required level of theory is still high. Indeed, at the ab initio level, a large basis set and the inclusion of electron correlation have been found to be essential for a correct description of the third-order polarizability tensor components.[8,10,11,20−26] Besides an ab initio approach, it would thus be also useful to establish the reliability of a semiempirical approach that could be exploited on larger compounds.

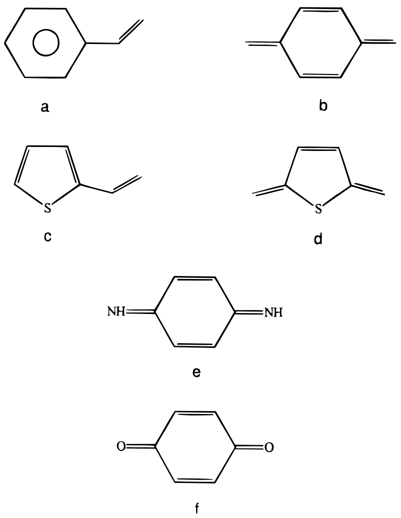


Figure 1. Molecular structure of (a) styrene, (b) 3,6-dimethylene-1,4-cyclohexadiene (or quinodimethane), (c) 2-ethenylthiophene, (d) bis(methylidene)-2,5-thiocyclopentene, (e) *p*-benzoquinone diimine, and (f) benzoquinone.

In this contribution, we evaluate at the ab initio and semiempirical levels the static first- and third-order polarizability tensor components of several conjugated cyclic molecules in either aromatic or quinoid geometric structures. The conjugated systems we consider are presented in Figure 1 and correspond to phenylene−ethenylene and thienylene−ethenylene compounds and their quinoid counterparts. (Note that in all cases the molecule lies in the *xy* plane with the *x* axis connecting the 1−4 [2−5] positions of the benzene [thiophene] compounds.) We perform high-level Hartree−Fock ab initio calculations complemented with second-order Møller−Plesset perturbation theory[27,28] as well as semiempirical intermediate neglect of differential overlap−configuration interaction (INDO-CI) calculations.[29,30] An attractive feature of these theoretical approaches is that they allow for inclusion of (part of) the electron correlation correction, either perturbatively or through a configuration interaction scheme. It is worth pointing out that relatively few ab initio evaluations of (hyper)polarizabilities with inclusion of electron correlation effects[20,24] have been reported for compounds of the size considered here, most dealing with smaller molecular systems.[10,25]

The objectives of this work are the following: (i) to analyze the impact of electron correlation on the (hyper)polarizability values, especially in the case of quinoid structures; (ii) to provide

---

[†] Université de Mons-Hainaut.

[‡] Pacific Northwest Laboratory.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S1089-5639(96)03012-5 CCC: $14.00

an accurate evaluation of the optical nonlinearities in monomeric structures, in order to help in the design of novel classes of NLO materials; (iii) to establish the validity of the semiempirical INDO/CI method to estimate the γ response; and (iv) to identify the relationships between the molecular architecture and the (hyper)polarizability values, in particular the effect of aromaticity vs quinoidicity on the cubic nonlinearities. A quinoid geometric structure has often been considered as potentially leading to large nonlinear optical responses.[31,32]

Theoretical Approach

We have carried out full geometry optimizations for all the molecules at the restricted Hartree−Fock (RHF) ab initio level with a split-valence 3-21G basis set. The latter represents a good compromise between quality of results and computational time.[33] It is interesting to mention that the geometric structure of several molecules considered in this work have also been optimized using more extended basis sets;[34] the results indicate that the calculated (hyper)polarizability tensor components are not affected in any significant way by the inclusion of polarization and/or diffuse functions during the geometry optimizations. Therefore, for the sake of ease of comparison, all the optimized molecular geometries in this work are based on the standard 3-21G basis set.

The static (hyper)polarizability tensor components are then evaluated in the framework of the second-order Møller−Plesset (MP2) perturbation theory by the finite field (FF) method.[35] Note that, as previously shown for the total energy and NLO coefficients of smaller molecules,[10,36] the major contribution of the total electron correlation correction is expected to be provided at the MP2 level. We employ a general formalism, originally proposed to evaluate the longitudinal hyperpolarizabilities of *p*-nitroaniline,[24] that we have extended to describe all the components of the (hyper)polarizability tensors of the urea molecule.[36] The calculations have been performed using the parallel version of the HONDO set of programs,[37] which is well adapted to the description of extended compounds.

Many theoretical studies have revealed the importance of the basis set selection in the computation of the molecular optical nonlinearities. The extent of the basis set drastically influences the third-order polarizability values, the use of diffuse functions being crucial.[8,9,20−22] According to our previous calculations where the efficiency of different basis sets including polarization and diffuse functions has been examined,[34] we have selected the basis set labeled 3-21G + pd. This basis set appears appropriate to obtain reliable trends for the cubic polarizabilities of organic molecules of the size considered here. It corresponds to the standard 3-21G basis set to which one p and one d function (ζ exponent = 0.05 for the carbon and nitrogen atoms; ζ = 0.04 for oxygen atom; ζ = 0.03 for sulfur atom) are added on "heavy" atoms.

Recall that in the presence of a strong (i.e., laser-generated) external electric field of strength F, the total energy E of the molecule can be written as a Taylor series expansion of the field:

$$E(F) = E^{(0)} - \sum_i \mu_i^{(0)} F_i - \frac{1}{2!}\sum_{ij} \alpha_{ij} F_i F_j - \frac{1}{3!}\sum_{ijk} \beta_{ijk} F_i F_j F_k - \frac{1}{4!}\sum_{ijkl} \gamma_{ijkl} F_i F_j F_k F_l - \ldots \quad (1)$$

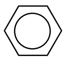
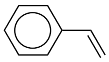
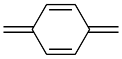
where α_{ij}, β_{ijk}, and γ_{ijkl} are the tensor components of the static first-, second-, and third-order dipole polarizabilities, respectively. The *ijkl* subscripts, which identify the tensor and field components, run over the Cartesian axes *x*, *y*, *z*. The $E^{(0)}$ and $\mu_i(0)$ terms correspond to the unperturbed total energy and permanent dipole moment component, respectively. (Note that for a comparison with experimental data where a power series expansion is usually considered α and γ need to be divided by 2 and 6, respectively.) The molecular polarizability of order n can then be obtained as the $(n + 1)$th-order derivative of the molecular total energy E (eq 1) with respect to the external electric field F or the nth-order derivation of the dipole moment, provided the Hellmann−Feynman theorem[38] is satisfied. Since this latter condition is not fulfilled for Møller−Plesset energies, we will base our calculations on the derivations of the energy expression.

The evaluation of these derivatives can be carried out analytically or numerically. A numerical procedure is used in the finite field approach; its main advantage is to allow for an easy introduction of electron correlation in the calculation. The accuracy of the finite field procedure has to be controlled by carefully choosing the field values and by keeping enough terms in the energy expression (eq 1). Instead of deriving μ, α, β, and γ in terms of energies perturbed by chosen *pairs* of applied electric field strengths (±mF), as for instance described by Kurtz et al.,[39] the coefficients of F are determined by solving a set of linear equations via the singular value decomposition (SVD) algorithm,[40] which is a powerful method for solving most linear least-squares problems. The latter is based on truncating the energy expression to an order n equal to 6 and evaluating the unperturbed energy $E^{(0)}$ as well as energies $E(F_i,F_j)$ calculated for different electric field strengths applied in a general direction of the *ij* plane;[36] this method is quite general and easily applicable to almost any quantum-chemical formalism where the total energy is determined in the presence of an electric field.

The selection of appropriate external electric field strengths, which is crucial to provide a correct estimate of the polarizabilities, was made according to the results of previous studies[21,24] and by performing some test calculations for the urea molecule.[36] About 37 energy points in the *xy*, *xz*, and *yz* planes are computed for electric field values ranging from 10^{-2} to 10^{-3} atomic unit (1 au of electric field = 5.14×10^9 V/cm). These values are high enough to achieve the required numerical accuracy in the energy calculation but not too large to contaminate the (hyper)polarizability values by higher-order terms. The validity of this numerical approach is examined for the benzene and thiophene derivatives at the self-consistent-field (SCF) Hartree−Fock level of theory, by comparison with analytical derivative results obtained within the time-independent coupled perturbed Hartree−Fock (CPHF) scheme.[41,42]

We perform the semiempirical (hyper)polarizability calculations on the aromatic and quinoid compounds in the framework of the INDO-CI technique using the ZINDO package[30] on the basis of the 3-21G optimized geometries. The CI employed here includes single (S) and double (D) excitations among all π molecular orbitals (SDCI calculation). It is interesting to mention that a reliable estimate of γ requires the treatment of the electron−electron interactions at least at an SDCI level of configuration interaction. (A single CI approach for instance provides spurious negative static γ values for benzene.[14]) The electronic Coulomb repulsion terms are expressed by the Ohno formula; this parametrization is well adapted when doubly excited configurations are included in the CI calculation.[11,14] The nonlinear optical coefficients α and γ of the benzene and thiophene derivatives are then obtained by applying the elegant correction vector (CV) approach. Introduced by Soos and

TABLE 1: Ab Initio Finite Field First- and Third-Order Polarizability Components Calculated by the SVD Fit to the SCF and MP2 Energy Expansions Using the Extended 3-21G + pd Basis Set for Benzene, Styrene, and Quinodimethane[a]

												
		finite field				finite field				finite field		
	CPHF	SCF	MP2	INDO SDCI	CPHF	SCF	MP2	INDO SDCI	CPHF	SCF	MP2	INDO SDCI
E_0	−229.449	−229.449	−229.998		−305.872	−305.872	−306.576		−305.880	−305.880	−306.605	
α_{xx}	10.94	10.94	11.21	4.61	18.16	18.15	18.11	6.18	29.07	29.07	24.19	13.73
α_{yy}	10.94	10.94	11.25	4.61	14.03	14.02	14.08	5.51	11.21	11.21	12.00	1.34
α_{zz}	5.69	5.70	5.95		7.44	7.43	7.78		7.65	7.65	8.01	
$\langle\alpha\rangle$	9.19	9.19	9.46		13.21	13.20	13.32		15.98	15.98	14.73	
γ_{xxxx}	7.07	7.06	9.52	5.23	25.66	25.63	35.37	19.58	16.73	16.26	89.82	80.71
γ_{xxyy}	2.36	2.35	3.17	1.74	2.56	2.57	5.12	3.65	8.27	8.28	10.02	2.85
γ_{yyyy}	7.07	7.06	9.52	5.23	7.12	7.12	10.40	8.92	7.15	7.14	10.50	6.20
γ_{xxzz}	3.03	3.01	4.03		5.00	4.94	6.55		9.85	9.54	12.60	
γ_{yyzz}	3.03	3.01	4.03		3.52	3.50	4.75		3.06	3.06	4.14	
γ_{zzzz}	5.70	5.70	6.97		7.21	7.22	8.87		7.71	7.74	9.72	
$\langle\gamma\rangle$	7.33	7.31	9.69		12.44	12.40	17.50		14.79	14.58	32.72	

[a] The analytical CPHF values and the semiempirical INDO-SDCI values are also included. E_0 (in au) refers to the unperturbed total energy; α and γ are expressed in 10^{-24} esu [$\alpha(10^{-24}$ esu$) = 0.1482\ \alpha$(au); α(au) $= 1.6488 \times 10^{-41}$ C^2 m^2/J], and 10^{-36} esu [$\gamma(10^{-36}$ esu$) = 0.5037 \times 10^3\ \gamma$(au); γ(au) $= 6.2354 \times 10^{-65}$ C^4 m^4/J^3], respectively.

Ramasesha,[43] this method has been recently incorporated into the intermediate neglect of differential overlap (INDO) semiempirical technique and tested with success in the case of *p*-nitroaniline[44] as well as other di- and hexasubstituted donor−acceptor benzene derivatives.[18]

Within a given configuration space, the CV method provides exact results that are equivalent to those obtained with the conventional sum-over-states (SOS) approach[45] when *all* excited states are taken into account in the SOS summation: in general, the difficult description of the excited states as well as their huge number usually leads one to apply a somewhat arbitrary truncation in the SOS expression of the NLO coefficients; however, the magnitude and the sign of γ strongly depend on the number of states considered. By evaluating the (hyper)polarizabilities on the basis of the *ground-state* eigenvalue, eigenvector, and permanent dipole moment, the CV method has been shown to provide, within a given configuration space, the exact results in a shorter computation time.[44]

Finally, note that the orientationally averaged polarizabilities $\langle\alpha\rangle$ and $\langle\gamma\rangle$ are defined respectively as

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

$$\langle\gamma\rangle = {}^1/_5[\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2(\gamma_{xxyy} + \gamma_{yyzz} + \gamma_{xxzz})]$$

Electron Correlation Effects

In Tables 1and 2, we compare the static first- and third-order polarizability components of the benzene and thiophene derivatives calculated (on the basis of the 3-21G optimized geometry) at the SCF-FF and MP2-FF levels, using the extended 3-21G + pd basis set. This allows us to explore the electron correlation dependence of the polarizability components, in particular for γ.

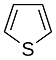
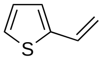
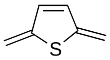
For the sake of comparison, we also report the corresponding values obtained with the coupled perturbed Hartree−Fock (CPHF) analytical approach using the same basis set; this method has to yield results equivalent to those obtained with the FF approach, provided the numerical procedure employed is valid. The SCF-FF α and γ values are indeed found to be in full agreement with the CPHF results. It is interesting to compare the $\langle\gamma\rangle$ value calculated for benzene with our numerical approach (9.7 × 10^{-36} esu), that of Perrin et al.[20] (10.2 × 10^{-36} esu) obtained with a different numerical procedure, a similar basis set (4-31G + pd), and a larger number of electric field points. For thiophene, essentially the same static $\langle\gamma\rangle$ value as ours, 7.3 × 10^{-36} esu, was obtained by Karna et al.[13] using time-dependent Hartree−Fock with a 4-31G basis set augmented with diffuse functions. (Note that, due to the choice of a different convention for the field expansion, the numeric values for γ in ref 13 should be multiplied by 6 to be compared with our results.) The efficiency of the finite field technique used being established, we now turn to the analysis of the electron correlation effects on the nonlinear optical properties of the cyclic conjugated molecules sketched in Tables 1 and 2.

The calculated α values are in good agreement with the available experimental data. (The off-resonance experimental $\langle\alpha\rangle$ values for benzene and thiophene are 10.4 × 10^{-24} esu and 9.6 × 10^{-24} esu, respectively).[20,46] As shown previously, this agreement comes from the use of diffuse functions in the basis set; in addition, the use of more extended basis sets allows to come even closer to the experimental values.[47−49]

The linear polarizabilities α do not change much with the introduction of the electron correlation correction. For instance, from SCF to MP2, the $\langle\alpha\rangle$ values evolve from 13.2 × 10^{-24} esu to 13.3 × 10^{-24} esu for styrene and from 15.9 × 10^{-24} to 14.7 × 10^{-24} esu for quinodimethane. In all compounds considered, the average $\langle\alpha\rangle$ value fluctuates by a maximum of 8%. Hinchliffe and Soscùn[47,48] as well as Stanton and Bartlett[49] have reached the same conclusion: the former from their studies of the polarizability of ethene, benzene, thiophene, and other five-membered heterocycles at the Hartree−Fock and MP2 levels and the latter from a comparison of the SCF and CCSD calculated α values for benzene. The effect is more pronounced for the quinoid compounds, due to a significant lowering of the longitudinal component: correlation reduces α_{xx} by about 17% in quinodimethane and 11% in bis(methylidene)-2,5-thiocyclopentene, i.e. from 29.1 × 10^{-24} to 24.2 × 10^{-24} esu and from 23.7 × 10^{-24} to 21.2 × 10^{-24} esu, respectively. (It is of major interest to analyze the evolution of the longitudinal components because these totally dominate the $\langle\alpha\rangle$ and $\langle\gamma\rangle$ responses in long chains.)

As expected, the impact of electron correlation is very important on the third-order polarizabilities γ. In going from the HF to the MP2 results, all the components significantly increase. In the cases of benzene and thiophene, we observe an increase in $\langle\gamma\rangle$ by 30 and 40%, respectively. The cubic polarizabilities of styrene and 2-ethenylthiophene are also enhanced by about 40%, the longitudinal γ_{xxxx} components going

TABLE 2: Ab Initio Finite Field First- and Third-Order Polarizability Components Calculated by the SVD Fit to the SCF and MP2 Energy Expansions Using the Extended 3-21G + pd Basis Set for Thiophene, 2-Ethenylthiophene, and Bis(methylidene)-2,5-thiocyclopentene[a]

												
		finite field				finite field				finite field		
	CPHF	SCF	MP2	INDO SDCI	CPHF	SCF	MP2	INDO SDCI	CPHF	SCF	MP2	INDO SDCI
E_0	−548.507	−548.507	−548.944		−624.977	−624.977	−625.597		−624.971	−624.971	−625.589	
α_{xx}	9.34	9.34	9.71	2.41	15.66	15.64	15.79	4.77	23.71	23.71	21.21	10.16
α_{yy}	10.49	10.49	10.69	3.55	14.77	14.76	14.30	5.54	11.23	11.23	11.96	1.78
α_{zz}	5.48	5.48	5.89		7.23	7.23	7.72		7.25	7.25	7.78	
$\langle\alpha\rangle$	8.44	8.44	8.76		12.55	12.55	12.60		14.06	14.06	13.65	
γ_{xxxx}	7.23	7.20	9.11	5.09	22.51	22.78	30.55	28.71	15.19	14.90	52.81	46.20
γ_{xxyy}	2.08	2.08	3.20	1.32	3.56	3.54	7.19	5.25	5.97	5.97	8.36	2.34
γ_{yyyy}	7.23	7.18	10.06	6.86	7.53	7.44	12.41	11.41	8.61	8.58	12.57	5.58
γ_{xxzz}	2.86	2.83	3.71		4.63	4.49	5.80		6.47	6.31	8.88	
γ_{yyzz}	2.96	2.92	3.98		3.89	3.85	5.13		3.04	3.01	4.36	
γ_{zzzz}	6.34	6.31	7.66		7.60	7.57	8.91		7.23	7.22	9.76	
$\langle\gamma\rangle$	7.32	7.32	9.72		12.36	12.31	17.62		12.40	12.26	23.67	

[a] The analytical CPHF values and the semiempirical INDO-SDCI values are also included. E_0 (in au) refers to the unperturbed total energy; α and γ are expressed in 10^{-24} esu [$\alpha(10^{-24}$ esu$) = 0.1482\ \alpha$(au); α(au) $= 1.6488 \times 10^{-41}$ C^2 m^2/J] and 10^{-36} esu [$\gamma(10^{-36}$ esu$) = 0.5037 \times 10^3\ \gamma$(au); γ(au) $= 6.2354 \times 10^{-65}$ C^4 m^4/J^3], respectively.

from 25.6 × 10^{-36} and 22.8 × 10^{-36} esu to 35.4 × 10^{-36} and 30.6 × 10^{-36} esu, respectively. The component most affected by inclusion of electron correlation is the nonaxial γ_{xxyy} component that doubles in the case of the arylethenyl type of structure.

In the corresponding quinoid systems, the correlated γ_{xxxx} values are calculated to be about 3−5 times larger than those obtained at the SCF level. For quinodimethane [bis(methylidene)-2,5-thiocyclopentene], the γ_{xxxx} component, which is equal to 16.3 × 10^{-36} esu [14.9 × 10^{-36} esu] at the SCF level, jumps to 89.8 × 10^{-36} esu [52.8 × 10^{-36} esu]. The other components increase by about 30−50% with correlation, which reinforces the effect observed along the *x* axis. Globally, there occurs an increase in average $\langle\gamma\rangle$ value by a factor 2 with the introduction of the electron correlation correction, $\langle\gamma\rangle$ going from 14.6 × 10^{-36} to 32.7 × 10^{-36} esu for quinodimethane and from 12.3 × 10^{-36} to 23.7 × 10^{-36} esu for bis(methylidene)-2,5-thiocyclopentene. These results are fully consistent with those previously reported for *p*-nitroaniline[24] and urea,[36] as well as for smaller nonconjugated organic compounds.[25]

An important point to mention is the different sensitivity of the longitudinal γ_{xxxx} components to the electron correlation treatment for the aromatic compounds and their quinoid counterparts. As a consequence, it contributes to a reversal in the γ trends. In fact, the results obtained at the SCF level suggested a strong decrease of the γ_{xxxx} component when switching to the quinoid structure (25.7 × 10^{-36} esu for styrene vs. 16.2 × 10^{-36} esu for quinodimethane) while the correlated γ_{xxxx} value of quinodimethane is considerably larger than that of the arylethenyl structure (89.8 × 10^{-36} esu *vs* 35.4 × 10^{-36} esu). Thus, there is a poor description of γ_{xxxx} at the noncorrelated level for the quinoid structures. Similar conclusions can be drawn for the thiophene derivatives.

Our results reveal thus confirm that electron correlation has a large influence on the absolute value of the molecular hyperpolarizabilities, in particular for quinoid compounds. The SCF $\langle\gamma\rangle$ values are always smaller than those calculated at the MP2 level. The range of these effects, however, strongly depends on the geometric and electronic structure of the organic compounds considered.

Influence of Molecular Architecture

In this section, we systematically examine at the ab initio level (the geometry optimizations being carried out at the Hartree−Fock ab initio level using the split-valence 3-21G basis set and the molecular polarizabilities α and γ evaluated via the MP2/FF correlated technique using the extended 3-21G + pd basis set) the nonlinear optical response of the conjugated molecules sketched in Figure 1. Our main concern here is to illustrate the influence of molecular architecture and thereby to provide useful information for the design of structures optimized for given third-order nonlinear optical applications. We pay special attention to the quinoid structures, *i.e.*, to the evolution of γ values with quinoidicity; besides quinodimethane, we also investigate the *p*-benzoquinone diimine and benzoquinone molecules, where nitrogen and oxygen atoms cap the conjugation path. Since polyenes are considered as the prototypical π-conjugated systems, we also perform similar calculations for octatetraene, the π isoelectronic counterpart of quinodimethane, as well as for its heteroatomic derivatives; see Figure 2.

The results are reported in Tables 1, 2, and 3. As expected, with the addition of a double bond to the benzene ring, we observe a large enhancement of the average α and γ values: $\langle\alpha\rangle$ evolves from 9.5 × 10^{-24} to 13.3 × 10^{-24} esu and $\langle\gamma\rangle$ from 9.7 × 10^{-36} esu to 17.5 × 10^{-36} esu. The longitudinal $\langle\gamma\rangle$ component is the most affected: it approximately quadruples (35.4 × 10^{-36} esu in styrene against only 9.5 × 10^{-36} esu in benzene), a feature in relation with an easier electron delocalization along the main axis for arylethenyl molecules. This effect is less marked for the linear polarizability: α_{xx} increases by about 60% with ethenyl substitution. It is worth noting that the effect of an extra double bond goes beyond the simple addition of two more π-electrons to the molecule, especially in the case of γ. (The calculated $\langle\alpha\rangle$ and $\langle\gamma\rangle$ (γ_{xxxx}) values of ethylene are equal to 3.6 × 10^{-24} esu and 3.5 × 10^{-36} esu (1.6 × 10^{-36} esu), respectively.)

The comparison of the first- and third-order polarizability components of styrene with those obtained for its quinoid-like isoelectronic counterpart, quinodimethane, indicates a significant enhancement of the intrinsic α and γ values with quinoidicity. The α_{xx} component is enhanced by about 33% while γ_{xxxx} increases by a factor 2.5. This effect, previously reported for α,[31] can only be observed for γ when introducing (a significant part of) the electron correlation correction that has a considerable impact on the NLO response of quinoid compounds. The same conclusions are reached from the results obtained for thiophene-based molecules (see Table 2); note that the magnitude of γ is larger for the quinoid benzene derivatives. The switch from a

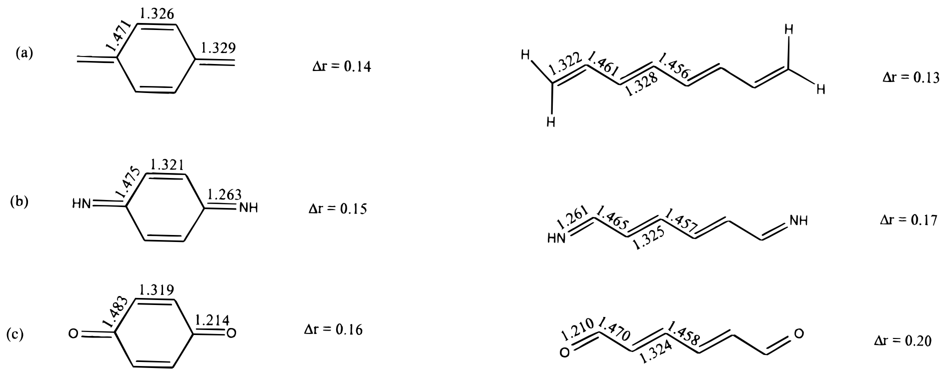
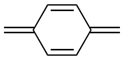
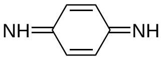
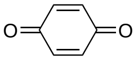
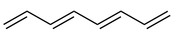
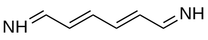
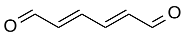


Figure 2. Optimized RHF/3-21G bond lengths (in Å) for (a) quinodimethane, (b) *p*-benzoquinone diimine, and (c) benzoquinone. For sake of comparison, the results obtained for octatetraene and its heteroatomic derivatives are also included. The Δ*r* parameter (in Å) is the average degree of bond-length alternation within the ring (see text) for the quinoid compounds or along the chain for the polyene compounds.

TABLE 3: MP2/FF ab Initio ⟨α⟩ (in 10^{-24} esu) and ⟨γ⟩ (in 10^{-36} esu) Values and Their In-Plane Tensor Components for Quinodimethane, *p*-Benzoquinone Diimine, and Benzoquinone; Values for Octatetraene as Well as Its Heteroaromatic Derivatives Are Also Reported

			
α_{xx}	24.19	19.20	15.43
α_{yy}	12.00	10.53	9.30
$\langle\alpha\rangle$	14.73	12.19	10.16
γ_{xxxx}	89.82	35.48	8.97
γ_{xxyy}	10.02	8.06	5.14
γ_{yyyy}	10.50	11.16	7.87
$\langle\gamma\rangle$	32.72	17.16	7.72

			
α_{xx}	30.55	25.80	21.76
α_{yy}	11.87	10.86	9.58
$\langle\alpha\rangle$	17.01	14.69	12.51
γ_{xxxx}	275.59	152.30	87.07
γ_{xxyy}	8.94	2.50	1.37
γ_{yyyy}	8.48	10.87	8.09
$\langle\gamma\rangle$	69.06	39.05	27.81

purely aromatic structure to a quinoid structure thus appears as a right move to boost the third-order polarizabilities.

We next focus our attention on the molecular polarizabilities calculated for quinodimethane and its substituted derivatives (see Table 3). The γ values are more affected by the substitution and geometry modifications than the linear polarizabilities α. There is a marked decrease in γ when going from quinodimethane to benzoquinone. (The γ_{xxxx} component calculated at 89.8 × 10^{-36} esu for quinodimethane goes down to 35.5 × 10^{-36} esu for *p*-benzoquinone diimine and only reaches 9.0 × 10^{-36} esu for benzoquinone.) While γ evolves by 1 order of magnitude, the α values are calculated to be in the same range.

For the polyene-like molecules, similar trends are observed: the γ_{xxxx} component is equal to 275 × 10^{-36} esu for octatetraene vs only 152 × 10^{-36} and 87.1 × 10^{-36} esu for the substituted compounds. Despite the fact that these conjugated systems are π isoelectronic to the quinoid-type corresponding molecules, the γ_{xxxx} values are considerably larger for the linear conjugated backbone, which is more extended: 275 × 10^{-36} esu for octatetraene *vs* only 89.8 × 10^{-36} esu for quinodimethane. This again demonstrates the high efficiency of the polyene third-order nonlinear response. On the opposite, the α_{xx} components remain of the same order of magnitude (30.6 × 10^{-24} esu compared to 24.2 × 10^{-24} esu). This illustrates the more local character of the linear polarizability.

The marked evolution of the γ values upon substitution, be it in the quinodimethane or polyenes series, can be correlated to geometric structure modifications. The molecular structure and optimized RHF/3-21G bond lengths for the quinoid compounds and the corresponding polyene-like molecules are presented in Figure 2.

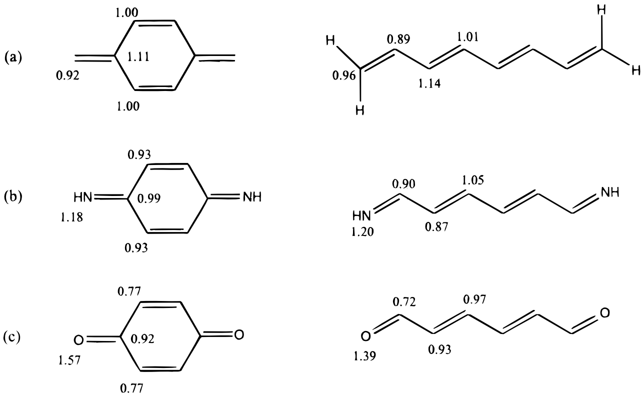


Figure 3. π-charge distributions (in electron charge unit |*e*|) as provided by a Mulliken population analysis (3-21G + pd basis set) for (a) quinodimethane, (b) *p*-benzoquinone diimine, and (c) benzoquinone.

One way to characterize the geometry evolution is to examine the average degree of bond-length alternation Δ*r*. In the quinoid compounds, this parameter is defined as (see Figure 2) the average of the difference in length between the 2−3 inclined C−C bond and, on one hand, the 1−2 horizontal C−C bond and, on the other, the 3−4 horizontal C−C bond. The values of Δ*r* are calculated for quinodimethane, *p*-benzoquinone diimine, and benzoquinone to be 0.14, 0.15, and 0.16 Å, respectively. This translates an increase in quinoid character within the ring. In the same way for polyene-like molecules, we observe a significant Δ*r* increase (defined here as the average difference between single and double C−C bonds) along the conjugated framework related to the presence of nitrogen and oxygen atoms: from 0.13 to 0.20 Å.

It clearly appears that the larger the degree of bond-length alternation, the smaller the third-order polarizabilities. This result is fully consistent with the results from Marder and coworkers, who have modulated Δ*r* experimentally by modifying the polarity of the solvent[16,50] or theoretically by the application of an external electric field.[17]

In order to rationalize the geometry evolutions described above, we have also investigated the ab initio π-charge distributions (as provided by a Mulliken population analysis). These are illustrated in Figure 3. An important localization of the π-charge on the nitrogen and oxygen atoms of *p*-benzoquinone diimine and benzoquinone leads to a π-charge deficit on the quinoid ring. The heteroatoms thus play the role of π-electron acceptors and anchor part of the π-electron cloud, which limits the capacity of π-charge delocalization. For the polyene-like molecules, the effect is found to be almost identical.

Finally, we mention that one has to be cautious when applying the scaling laws that would predict a parallel evolution for α and γ when one extrapolates the γ values from the α values. Indeed, the $\langle\alpha\rangle$ value of benzene (9.5×10^{-24} esu) is slightly smaller than that of benzoquinone (10.2×10^{-24} esu) while the third-order polarizability $\langle\gamma\rangle$ is larger (9.7×10^{-36} compared to 7.7×10^{-36} esu). The calculated trend in $\langle\gamma\rangle$ is in qualitative agreement with the degenerate four-wave mixing (DFWM) experimental $\langle\gamma\rangle$ values measured for benzene and benzoquinone.[51,52]

Comparison of INDO and ab Initio Results

Accurate calculations of molecular polarizabilities are not feasible for long-chain molecules; hence, simplified methods have to be used. In this section, we examine the ability of the semiempirical INDO-CI approach in reproducing the results of correlated ab initio calculations.

In Tables 1 and 2, we compare the α and γ values of the aromatic and quinoid benzene and thiophene derivatives obtained from the INDO-CI/CV method with the corresponding ab initio MP2/FF values using the 3-21G + pd basis set. We only list the in-plane components; the INDO transverse components are less well reproduced because of the small size (minimal) of the basis set used at the semiempirical level.

In general, in absolute terms, the INDO-CI/CV results consistently provide smaller longitudinal γ_{xxxx} components than the corresponding MP2/FF ab initio values. Nevertheless, the trends observed at the ab initio level for the first- and third-order polarizabilities are well reproduced by the semiempirical calculations, in particular for the longitudinal components (the most important one when the chain length is increased); the major difference occurs for styrene where the INDO γ_{xxxx} component is calculated to be too small. Otherwise, the trends provided by the INDO results are the same as at the ab initio level: (i) There is a major increase in the γ value when linking an ethenyl group onto the aromatic rings (thiophene or benzene); the linear polarizabilities also increase but again appear to be less sensitive to this effect. (ii) The quinoid compounds are seen to be more efficient than their aromatic counterparts.

The overall agreement with the ab initio values can thus be considered as very good, especially for quinoid compounds even though the INDO Hamiltonian is semiempirical, the CV method corresponds to an uncoupled approach, and the basis set does not include diffuse functions. It is worthwhile to mention that the basis set effects are expected to decrease with chain length extension;[8] this can contribute to reduce the differences between the semiempirical and ab initio (hyper)polarizability values in longer conjugated systems.

We thus believe that, by leading to first- and third-order polarizability values comparable to those obtained via a more accurate ab initio method, such as the MP2/FF technique, the INDO method coupled with the CV technique provides a useful alternative to ab initio calculations in order to investigate the trends in molecular polarizabilities for long conjugated systems. The active configuration space for the CV calculations has, of course, to grow with chain extension, a feature which will also eventually provide size limitations.

Synopsis

We have reported Møller−Plesset ab initio 3-21G + pd calculations on the first- and third-order polarizabilities of a series of benzene and thiophene derivatives presenting either aromatic or quinoid structures. A general finite field method, previously employed in the case of *p*-nitroaniline and urea, has been applied to explore the electron correlation effects on the nonlinear optical response of medium-size molecules. In order to test the validity of the numerical procedure, we have compared our results with those obtained with the coupled perturbed Hartree−Fock (CPHF) analytical approach using the same basis set.

We have shown that in a series of chemically related compounds the correlation effects significantly affect not only the absolute values of the third-order polarizabilities but also the trends among the series of compounds we have investigated. This is due to the fact that the electron correlation treatment has a larger impact on the quinoid structure than on the corresponding aromatic cyclic compounds. The range of electron correlation effects thus depends on the type of structure considered; this is consistent with previous results reported for organic compounds such as benzene,[20] *p*-nitroaniline,[24] urea[25] and nonconjugated small molecules.[36]

This work also indicates a significant increase in α and γ values with quinoidicity. An important point to stress here is that, for the third-order polarizabilities, this effect can actually only be observed when including the electron correlation correction (that is higher in quinoid structures). Within a series of quinoid compounds (quinodimethane and its substituted derivatives, *p*-benzoquinone diimine and benzoquinone), the anchoring effects of the nitrogen and oxygen atoms are seen to reduce the polarizabilities (as well as to increase the degree of bond-length alternation).

Finally, through a comparison of the ab initio MP2 results with those obtained from an INDO-CI approach coupled with the correction vector method, we have shown the ability of the semiempirical technique in reproducing the trends in correlated ab initio γ values. The INDO-CI/CV approach thus appears promising to obtain reliable estimates of the static and dynamic nonlinear optical properties of large-size molecules.

Acknowledgment. The NLO work in Mons is partly supported by the Belgian Prime Minister Office of Science Policy (SSTC) “Pôle d’Attraction Interuniversitaire en Chimie Supramoléculaire et Catalyse”, an IBM Academic Joint Study, FNRS-FRFC, and the European Commission (Human Capital and Mobility Networks “Synthetic Electroactive Materials (SELMAT)” and “New Third-Order Nonlinear Optical Molecular Materials”).

References and Notes

(1) Chemla, D. S.; Zyss, J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987; Vols. 1 and 2.

(2) Brédas, J. L.; Chance, R. R. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics*; Kluwer: Dordrecht, 1990.

(3) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, 1991.

(4) Marder, S. R.; Sohn, J. E.; Stucky, G. D. *Materials for Nonlinear Optics* American Chemical Society: Washington, DC, 1991.

(5) Ashwell, G. J.; Bloor, D. *Organics Materials for Non-linear Optics III*; Royal Society of Chemistry: Cambridge, 1993.

(6) Brédas, J. L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. *Chem. Rev.* **1994**, *94*, 243.

(7) Möhlmann, G. R. Nonlinear Optical Properties of Organic Materials VII. *SPIE-Int. Soc. Eng. Opt. Eng.* **1994**, *2285*.

(8) Hurst, G. J. B.; Dupuis, M.; Clementi, E. *J. Chem. Phys.* **1988**, *89*, 385.

(9) Daniel, C.; Dupuis, M. *Chem. Phys. Lett.* **1990**, *17*, 209.

(10) Sekino, H.; Bartlett, R. J. *J. Chem. Phys.* **1991**, *94*, 3665.

(11) Archibong, E. F.; Thakkar, A. J. *J. Chem. Phys.* **1993**, *98*, 8324.

(12) Kirtman, B.; Toto, J. L.; Robins, K. A.; Hasan, M. *J. Chem. Phys.* **1995**, *102*, 5350.

(13) Keshari, V.; Wijekoon, W. M. P.; Prasad, P. N.; Karna, S. P. *J. Phys. Chem.* **1995**, *99*, 9045.

(14) Pierce, B. M. *J. Chem. Phys.* **1989**, *91*, 791.

(15) Matsuzawa, N.; Dixon, D. A. *J. Phys. Chem.* **1992**, *96*, 6232. Matsuzawa, N.; Dixon, D. A. *Int. J. Quantum Chem.* **1992**, *44*, 497.

(16) Marder, S. R.; Perry, J. W.; Bourhill, G.; Gorman, C. B.; Tiemann, B. G.; Mansour, K. *Science* **1993**, *261*, 186.

(17) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. L. *J. Am. Chem. Soc.* **1993**, *116*, 10703.

(18) Shuai, Z.; Ramasesha, S.; Brédas, J. L. *Chem. Phys. Lett.* **1996**, *250*, 14.

(19) Shuai, Z.; Brédas, J. L. *Phys. Rev. B* **1991**, *44*, 5962. Shuai, Z.; Brédas, J. L. *Phys. Rev. B* **1992**, *46*, 4395.

(20) Perrin, E.; Prasad, P. N.; Mougenot, P.; Dupuis, M. *J. Chem. Phys.* **1989**, *91*, 4728.

(21) Chopra, P.; Carlacci, L.; King, H. F.; Prasad, P. N. *J. Phys. Chem.* **1989**, *93*, 7120.

(22) Spackman, M. A. *J. Phys. Chem.* **1989**, *93*, 7594; *J. Chem. Phys.* **1991**, *94*, 1288.

(23) Jaszunski, M.; Jørgenssen, P.; Jensen, H. J. A. *Chem. Phys. Lett.* **1992**, *191*, 293.

(24) Sim, F.; Chin, S.; Dupuis, M.; Rice, J. E. *J. Phys. Chem.* **1993**, *97*, 1158.

(25) Das, G. P.; Yeates, A. T.; Dudis, D. S. *Chem. Phys. Lett.* **1993**, *212*, 671.

(26) Lauderdale, W. J.; Coolidge, M. B. *J. Phys. Chem.* **1995**, *99*, 9368.

(27) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618.

(28) Paldus, J.; Cizek, J. *Adv. Quantum Chem.* **1975**, *9*, 105. Kapuy, E.; Csepses, I.; Kozmutza, C. *Int. J. Quantum Chem.* **1983**, *23*, 1981. Pople, J. A.; Frisch, M. J.; Luke, B. T.; Binkley, J. S. *Int. Quantum Chem., Quantum Chem. Symp.* **1983**, *17*, 307. Ladik, J. J. *Quantum Theory of Polymers as Solids*; Plenum: New York, 1988.

(29) Pople, J. A.; Beveridge, D. L.; Dobosh, P. A. *J. Chem. Phys.* **1967**, *47*, 2026.

(30) Ridley, J.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111.

(31) Brédas, J. L.; Dory, M.; Thémans, B.; Delhalle, J.; André, J. M. *Synth. Met.* **1989**, *28*, D533.

(32) Jenekhe, S. A.; Lo, S. K.; Flom, S. R. *Appl. Phys. Lett.* **1989**, *54*, 2524.

(33) Dykstra, C. E. *Ab Initio Calculations of the Structures and Properties of Molecules*; Elsevier: Amsterdam, 1988.

(34) Adant, C.; Brédas, J. L. *Nonlinear Opt.* **1994**, *8*, 87.

(35) Cohen, H. D.; Roothaan, C. C. J. *J. Chem. Phys.* **1965**, *43*, S34.

(36) Adant, C.; Dupuis, M.; Brédas, J. L. *Int. J. Quantum Chem.* **1995**, *29*, 497.

(37) Dupuis, M.; Johnson, F.; Marquez, A. *HONDO 8.5 from CHEM-Station*; IBM Corporation: Kingston, NY, 1994.

(38) Feynman, R. P. *Phys. Rev.* **1939**, *56*, 340. Hellmann, H. *Die Entführung in die Quantenchemie*; Franz Deuticke: Leipzig, 1937.

(39) Kurtz, H. A.; Steward, J. J. P.; Dieter, K. M. *J. Comput. Chem.* **1990**, *11*, 82.

(40) Press, W. H.; Finney, B. P.; Teukolsky, S. A.; Vettering, W. T. *Numerical Recipes*; (Cambridge University Press: Cambridge, U.K., 1989.

(41) Pulay, P. *J. Chem. Phys.* **1983**, *78*, 5043.

(42) Dykstra, C. E.; Jasien, P. G. *Chem. Phys. Lett.* **1984**, *109*, 388.

(43) Soos, Z. G.; Ramasesha, S. *J. Chem. Phys.* **1989**, *90*, 1067.

(44) Ramasesha, S.; Shuai, Z.; Brédas, J. L. *Chem. Phys. Lett.* **1995**, *245*, 224.

(45) Orr, J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513.

(46) Zhao, M. T.; Singh, B. P.; Prasad, P. N. *J. Chem. Phys.* **1989**, *89*, 5535.

(47) Hinchliffe, A.; Soscùn, H. J. M. *J. Mol. Struct. (THEOCHEM)* **1994**, *300*, 1.

(48) Hinchliffe, A.; Soscùn, H. J. M. *J. Mol. Struct. (THEOCHEM)* **1995**, *331*, 109.

(49) Stanton, J. F.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *99*, 5178.

(50) Gorman, C. B.; Marder, S. R. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 11297.

(51) Zhao, M. T.; Samoc, M.; Singh, B. P.; Prasad, P. N. *J. Phys. Chem.* **1989**, *93*, 7916.

(52) Tackx, P.; Derhaeg, L.; Persoons A. Personal communication.