J. Am. Chem. Soc. **1994**, *116*, 2094–2102

Theoretical and Experimental Investigations of the Nonlinear Optical Properties of Vanillin, Polyenovanillin, and Bisvanillin Derivatives

Chantal Andraud,[*,†] Thierry Brotin,[†] Chantal Garcia,[†] Fabienne Pellé,[‡] Philippe Goldner,[‡] Bernard Bigot,[§] and André Collet[*,†]

Contribution from the Ecole normale supérieure de Lyon, laboratoire de Stéréochimie et des Interactions moléculaires, and laboratoire de Chimie théorique, 69364 Lyon Cedex 07, France, and laboratoire de Physicochimie des matériaux, CNRS, 92190 Meudon Cedex, France

Received June 28, 1993. Revised Manuscript Received December 10, 1993[•]

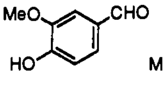
Abstract: The potential interest of *vanillin, isovanillin, thiovanillin,* and *isothiovanillin* as starting units for the design of hyperpolarizable molecules such as *polyenovanillin* (Ar–(CH═CH)$_n$—CH═O) and *bisvanillin* derivatives was investigated by a CNDO/S method using a specific program that allowed the calculation of all the components of the first-order molecular hyperpolarizability tensor β in nonpolar solvents. The reliability of the calculations was assessed by comparison with EFISH measurements on model systems. Among the vanillin derivatives, thiovanillin, where the sulfur group is in *para* to the aldehyde group, showed the largest hyperpolarizability, β. In polyenovanillins, the magnitude of β was predicted to increase as m^2 (m being the number of unsaturated bonds between the donor substituents of the aromatic ring and the aldehyde group), without saturation effect on the hyperpolarizability density $\rho = \beta/V$ at least up to $m = 9$. The calculations indicated that the thiovanillyl group (and its S-alkylated derivatives) was equivalent to the *p*-(dimethylamino)phenyl group in its ability to enhance the hyperpolarizability of polyenic systems, a result which may have important practical consequences. In bisvanillin, for torsion angles between the benzene rings greater than 25°, the magnitude of β was calculated to be the vector addition of the contributions of the monomer units, while for smaller angles, approaching planarity (in the *cisoid* conformation), a significant enhancement due to the conjugation of the two benzene rings was evidenced. It was concluded from this analysis that polyenovanillin and bisvanillin derivatives represent an interesting new family of hyperpolarizable molecules for applications in nonlinear optics.

I. Introduction

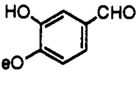
Organic molecules with delocalized π-electron systems may display large nonlinear responses[1] which make them attractive for applications in integrated optics such as, for instance, frequency doubling of semiconductor lasers and electrooptic modulation of light. For second-order processes, the optimization of the nonlinear optical properties of organic materials requires the knowledge of the first-order molecular hyperpolarizability $\beta(-2\omega,\omega,\omega)$. Three main factors have been identified to play an important role on the magnitude of β, namely, (a) the presence of donor and acceptor substituents in the molecule, (b) the nature and relative position of these substituents and their ability to promote charge transfer transitions between them, and (c) the extension of the conjugated path through which electrons are transfered under the influence of electric fields.

During the last two decades, a variety of hyperpolarizable molecules bearing donor and acceptor substituents have been studied and, at first sight, the chance to discover *new simple structures* that would meet the above requirements may seem low. Yet, the potential usefulness of vanillin (**1**) and isovanillin (**2**) (Chart 1), which are readily available and inexpensive materials, does not seem to have been considered in this context. In these substances, donor (OH and OMe) and acceptor (CH═O) groups are already present, and these groups lend themselves to simple chemical transformations that may enhance their hyperpolarizability properties. For instance, we have recently described a simple procedure for the conversion of **1** and **2** to thiovanillin (**3**) and isothiovanillin (**4**), and in turn to S-alkylated derivatives such as **5** and **6**.[2,3]

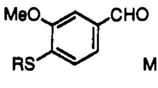
Chart 1



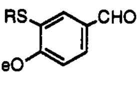
1



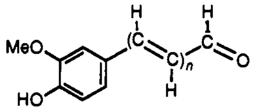
2



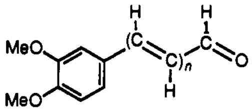
3 R=H
5 R=Me



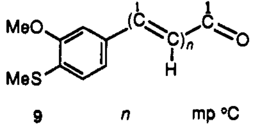
4 R=H
6 R=Me



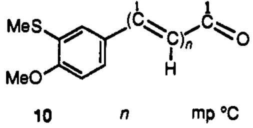
7	*n*	mp °C
7a	1	178



8	*n*	mp °C
8a	1	84
8b	2	90
8c	3	135
8d	4	176
8e	5	207d



9	*n*	mp °C
9a	1	91
9b	2	81
9c	3	127
9d	4	167
9e	5	197d



10	*n*	mp °C
10a	1	97
10b	2	120
10c	3	132
10d	4	172
10e	5	204d

[†] Stéréochimie et Interactions moléculaire (CNRS UMR 117).
[‡] Physicochimie des matériaux (CNRS UPR 211).
[§] Chimie théorique (CNRS UPR 5401).
[•] Abstract published in *Advance ACS Abstracts*, February 1, 1994.

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

[2] Garcia, C.; Andraud, C.; Collet, A. *Supramol. Chem.* **1992**, *1*, 31.

0002-7863/94/1516-2094$04.50/0 © 1994 American Chemical Society

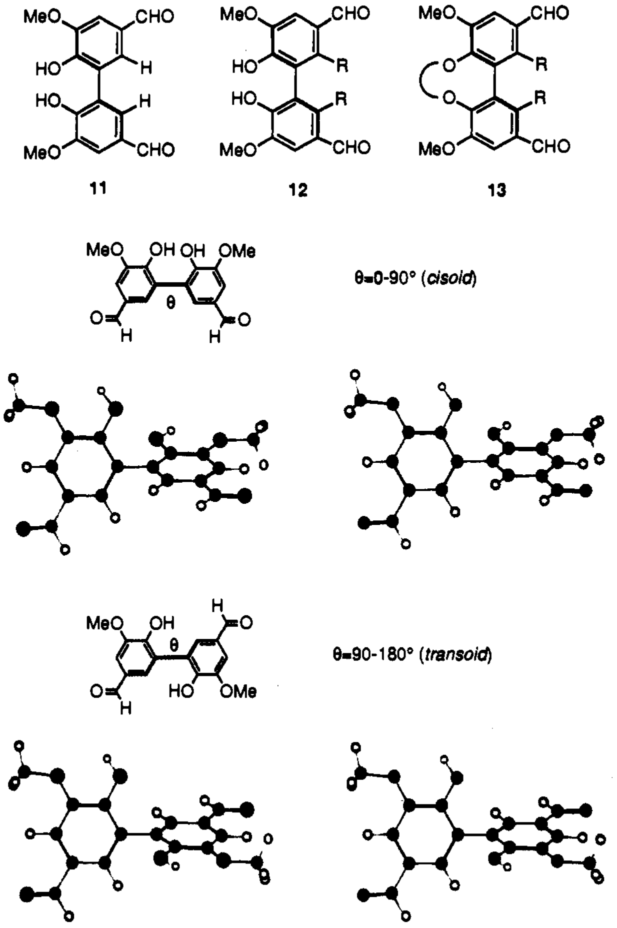
In order to increase the conjugation length, the aldehyde functions of **1–6** can be used to build polyenic chains, giving rise to *polyenovanillins*. To our knowledge, with the exception of the first member (**7a**, $n = 1$, coniferaldehyde), no examples of polyenoivanillins of structure **7** have been described so far. The syntheses of a few examples of compounds belonging to category **8** have been reported in a different context (**8a-d**).[4] In connection with the work reported here, we have examined various synthetic strategies allowing us to perform the homologation of CH=O to $(CH{=}CH)_n{-}CH{=}O$ in vanillin and thiovanillin derivatives. By using the methodology of L. Duhamel,[5] in which several double bonds are added in a single stage, polyenovanillins **8a–10e** could be obtained in pure *all-trans* form as nice crystalline materials (mp's indicated in Chart 1). These experiments also indicated that polyenovanillins with large conjugation paths show reasonably good stabilities.[6]

Since second-order nonlinear optic effects are only observed in acentric materials, a simple way to meet this condition is to use chiral molecules, or achiral molecules that crystallize in acentric space groups.[7] In this respect, vanillin displays an additional advantage; it can be easily dimerized to bisvanillin[8] (**11**) (Chart 2), which in turn lends itself to the same type of chemical transformations as described above for vanillin and its congeners. Bisvanillin itself is in principle chiral by atropoisomery; its most stable conformations are nonplanar, with a torsion angle θ of 120° (*transoid*) or 60° (*cisoid*) as shown in Chart 2. The rotation barrier, however, is not high enough to allow the existence of stable enantiomers in solution. Stable enantiomers should be accessible by replacement of the *ortho* hydrogens by suitable R groups (structure **12**) and by means of bridged systems such as **13**. Bridged systems may also be useful to optimize the torsion angle between the phenyl rings to a value that maximizes the hyperpolarizability of the molecule, along the lines that are discussed below.

The purpose of this work was to provide a theoretical model allowing us to understand and predict the first-order hyperpolarizability properties of vanillin, polyenovanillin, and bisvanillin derivatives, in order to facilitate the design of such molecules for specific applications in nonlinear optics. To this end, we have developed a program based on the CNDO/S method, which offers the advantage of being able to treat routinely large molecules containing elements of the third row, such as sulfur. Details on the calculation method and, particularly, on the parametrization technique are given in section II. The reliability of this calculation procedure was assessed by comparison of the computed hyperpolarizabilities of relevant systems with experimental (EFISH) measurements. The experimental setup we used for the EFISH measurements is described in the Appendix.

In section III, we present a theoretical and experimental evaluation of the magnitude of β in vanillin and isovanillin derivatives **1–6**, which represent the basic structures in our studies. We conclude that the MeS substituent is more efficient than the MeO substituent in enhancing the hyperpolarizability of these molecules when it is located *para* to the acceptor group. In section IV, we analyze in detail the influence of the extension of the π-system on the hyperpolarizability of polyenovanillin models (**7**) with up to seven double bonds. We show that, when the number of double bonds increases, there is no saturation effect on the hyperpolarizability, the enhancement of which is due to the increase of the oscillator strength of the first transition, rather than to an increase of the charge transfer. In section V, we address the question of the variation of β as a function of the torsion angle between the two benzene units in bisvanillin (**11**). We show that for small torsion angles in the *cisoid* conformation of the biphenyl system the magnitude of β is substantially greater than the sum of the contribution of the monomer units, due to conjugation effects.

Chart 2. Structures of Bisvanillin Derivatives and Stereoviews of Minimized Structures (MMX Force Field) for the *Cisoid* and *Transoid* Conformers of **11**



The following notation will be used throughout the paper: β, first-order hyperpolarizability; β_{ijk}, components of the hyperpolarizability tensor; β_{vec}, vector part of the tensor calculated by CNDO/S; β_i, vector component of the tensor along $i = x, y$, or z; β_μ, projection of β_{vec} onto the ground state dipole moment μ; β^0, hyperpolarizability tensor in a static field ($\omega = 0$); $\beta^{2\omega}$, hyperpolarizability tensor at frequency ω; β_{exp}, hyperpolarizability measured by the EFISH method; β_{av}, averaged value of β_μ for an equilibrium mixture of conformers (Boltzmann distribution).

II. Theoretical Calculations

For the calculation of the first-order hyperpolarizability tensor β, we developed a program based on the CNDO/S method[9] and derived from the QCPE 382 version.[10] The β_{ijk} components of the tensor were obtained

---

[3] In certain aromatic systems, thiol and thiomethyl groups have been shown to be good electron donors, see: (a) Barzoukas, M.; Josse, D.; Zyss, J.; Gordon, P.; Morley, J. O. *Chem. Phys.* **1989**, *139*, 359. (b) Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339. (c) Cheng, L. T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.

[4] Makin, S. M.; Shavrygina, O. A.; Dobretsova, E. K.; Ermakova, G. A.; Dymshakova, G. M. *Zh. Org. Khim.* **1982**, *18*, 749.

[5] Duhamel, L.; Guillemont, J.; Le Gallic, Y.; Plé, G.; Poirier, J. M.; Romendec, Y.; Chabardes, P. *Tetrahedron Lett.* **1990**, *31*, 3129.

[6] Full details on the syntheses, structural characterizations, and photophysical properties of these compounds will be reported separately: Brotin, T.; Andraud, C.; Pellé, F.; Collet, A. To be published.

[7] Zyss, J.; Chemla, D. S.; Nicoud, J.-F. *J. Chem. Phys.* **1981**, *74*, 4800 (PMO). Oudar, J. L.; Hierle, R. *J. Appl. Phys.* **1977**, *48*, 2699 (MAP). Zyss, J.; Nicoud, J.-F.; Coquillay, M. *J. Chem. Phys.* **1984**, *81*, 4160 (NPP).

[8] Elbs, K.; Lerch, H. *J. Prakt. Chem.* **1916**, *93*, 1 (oxydative coupling of vanillin in the presence of ferric sulfate).

[9] Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807.

[10] François, P.; Carles, P.; Rajzmann, M. *J. Chim. Phys.* **1977**, *74*, 606. *Ibid.* **1979**, *76*, 328.

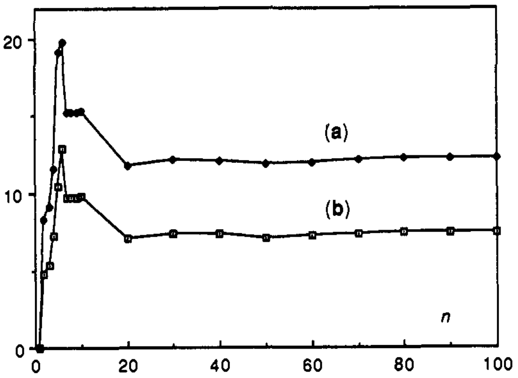


Figure 1. Convergence of $\beta_{vec}{}^0$ for two energies of the applied electric field: (a) $\hbar\omega$ = 1.17 eV and (b) $\hbar\omega$ = 0, for molecule **1**; n is the number of excited states taken into account in the calculation.

according to Pugh and Morley; the equation that we used[11] derives from the Ward perturbation theory[12] for the sum frequency generation ($\omega_\sigma = \omega_1 + \omega_2$) and is in fact equivalent to that given by Lalama and Garito.[13] The x, y, and z components (without Kleinman symmetry) were calculated from eq II-1, the calculated hyperpolarizability β_{vec} being finally obtained from eq II-2.

$$\beta_i = \beta_{iii} + \sum_{i \neq j}((\beta_{ijj} + 2\beta_{jji})/3) \qquad i = x, y, z \qquad \text{(II-1)}$$

$$\beta_{vec} = \sqrt{\beta_x{}^2 + \beta_y{}^2 + \beta_z{}^2} \qquad \text{(II-2)}$$

As the β component that is measured by the EFISH technique lies along the ground state dipole moment μ of the molecule, it was also necessary to calculate the correspond β_μ (projection of β_{vec} onto the axis of the dipole μ), which was done by using relation II-3, where each

$$\beta_\mu = \frac{\beta_x\mu_x + \beta_y\mu_y + \beta_z\mu_z}{\|\mu\|} \qquad \text{(II-3)}$$

component is given by eq II-1. In this treatment, the calculated values of β_μ are directly comparable to the experimental EFISH values, as detailed in the Appendix.

The energies of the excited states were evaluated by configuration interaction (CI)[14] restricted to the 100–150 lowest states, depending on the size of the molecules, until convergence of β_{vec} was obtained. For vanillin (**1**), Figure 1 shows the effect on β_{vec} of the successive consideration of the first lowest excited states up to 100. In general, good convergence was reached beyond 70 states.[15]

We examined the effect on β of two parametrization methods, differing only in the evaluation of the monocentric bielectronic Coulomb integrals Γ_{AA} and of the spectroscopic constants κ_p (Table 1). In both methods, the bicentric electron integrals were computed using the Nishimoto–Mataga approximation.[16] The calculations were checked against experimental data (in the gas phase, when available, and in solution) relative to well-documented molecules used for second harmonic generation (Chart 3), such as p-nitroaniline (PNA, I),[17] p-nitrothioanisole (II),[3a] 4-(N,N-dimethylamino)-4'-nitrostilbene (DANS, III), and polyenic molecules (IV–X).[3c]

Table 1. Parameters Used in CNDO/S Calculations[a]

method	κ_p	κ_d	$-\beta_S{}^0$ (eV)	ζ_s	ζ_p	ζ_d
A	0.585					
B[b]	0.650[c]	0.3	18.15[d]	1.817	1.200	0.300

[a] $\beta_S{}^0$ is the bonding parameter, and $\zeta_{s,p,d}$ represents the orbital exponents of the sulfur atom; the spectroscopic constants κ_p and κ_d take into account σ/π orbitals and 3d orbitals. For the other parameters of the CNDO/S method, we used the standard values given in ref 9. [b] The constant C_{AA} (see text) was optimized to 9.00. [c] The values of C_{AA} and κ_p are similar to those given in ref 21. [d] $\beta_S{}^0$ was optimized to –24.00 eV by Morley et al. (ref 21b).

Chart 3

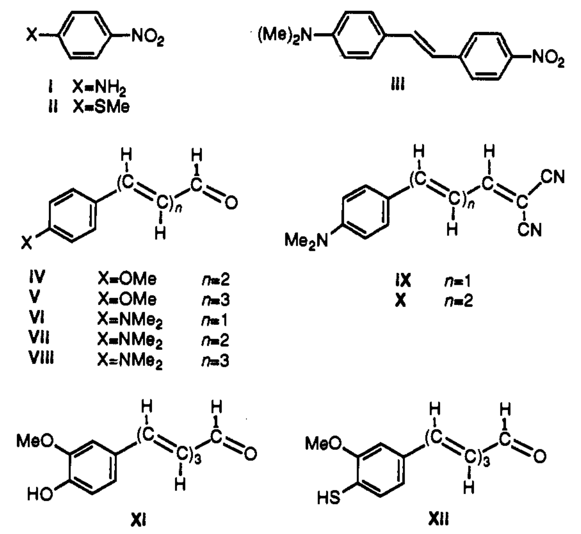


Table 2. Calculated and Experimental Data for Hyperpolarizable Molecules I–X[a]

	λ_{exp}	λ_{calcd}	μ_{exp}	μ_{calcd}	β_{exp}	β_μ	$\hbar\omega$
I[b]	321	320[g]	6.1	8.8	16.9	18.6	1.17
	285[e]	281[f]		7.4		7.6	
II[c]	335	343[g]	4.4	6.2	10.0	12.1	0
III[d]	430	413[g]	6.6	10.2	55.0	50.3	0
		341[f]		9.4		24.0	
IV[d]	350	385[g]	4.3	5.9	23.0	26.2	0
		318[f]		4.5		7.6	
V[d]	376	427[g]	4.6	6.5	34.0	43.8	0
VI[d]	384	365[g]	5.6	7.4	24.0	24.0	0
		296[f]		5.8		8.0	
VII[d]	412	410[g]	6.0	8.1	40.0	42.5	0
		326[g]		6.5		13.0	
VIII[d]	434	446[g]	6.3	8.5	66.0	65.0	0
IX[d]	486	450[g]	8.4	9.9	57.0	53.3	0
X[d]	520	482[g]	9.0	10.7	106.0	83.8	0
		377[f]		8.7		23.8	

[a] See structural formulas in Chart 3; λ_{exp} and λ_{calcd} (nm) are the experimental and calculated wavelengths of the lowest charge transfer state, μ_{exp} and μ_{calcd} (D) are the experimental and computed ground state dipole moments, and β_{exp} (10^{-30} esu) is the hyperpolarizability measured by the EFISH method, β_μ (10^{-30} esu) being the projection of the calculated hyperpolarizability tensor on μ_{calcd} direction. Experimental data are taken from [b]ref 17,[c] ref 3a, [d]ref 3c, [e]ref 19. [f] Parametrization A. [g] Parametrization B.

In the first parametrization method (hereafter called A), we adopted a set of standard CNDO/S values[9] for Γ_{AA} and κ_p, whereas in the second method (B), we computed the integrals Γ_{AA} according to the procedure described by François et al.[18] using eq II-4, where Φ_i and Φ_j represent atomic orbitals centered on atom A.

$$\Gamma_{AA} = C_{AA}\langle\Phi_i{}^2(1)|r_{12}{}^{-1}|\Phi_j{}^2(2)\rangle \qquad \text{(II-4)}$$

Parametrization A correctly reproduced the trend of the variations of μ, λ, and β for molecules devoid of sulfur atoms (Table 2), but the computed transition energies were too high, and for this reason, the calculated β

---

(11) Pugh, D.; Morley, J. O. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 1, pp 193–225. We specifically refer to eq 47, p 204, of this article.

(12) Ward, J. F. *Rev. Mod. Phys.* **1965**, *37*, 1. Ward, J. F.; New, G. H. C. *Phys. Rev.* **1969**, *185*, 57. Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513.

(13) Lalama, S. J.; Garito, A. F. *Phys. Rev. A* **1979**, *20*, 1179.

(14) Pariser, R. *J. Chem. Phys.* **1956**, *24*, 250.

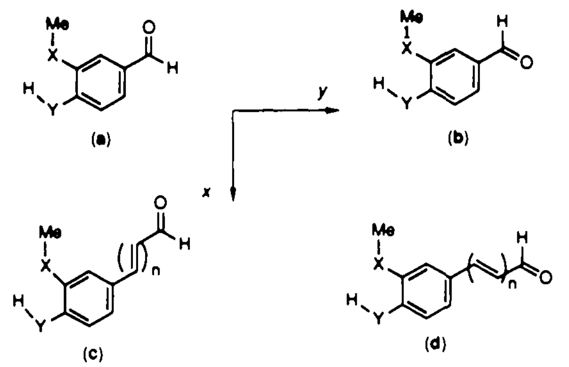
(15) Figure 1 is quite comparable with those reported, for instance, by Pugh and Morley for 4-nitroaniline and 4-amino-4'-nitrostilbene (ref 11) and shows that the contribution of the first charge transfer transition represents about 70% of the final value of β for this conformation of vanillin.

(16) Nishimoto, K.; Mataga, N. *Z. Phys. Chem.* **1957**, *12*, 335.

(17) (a) Teng, C. C.; Garito, A. F. *Phys. Rev. Lett.* **1983**, *50*, 350. (b) Teng, C. C.; Garito, A. F. *Phys. Rev. B* **1983**, *28*, 6766.

(18) In this case, constant C_{AA} is derived from a comparison of integrals calculated by a CNDO/2 method and those obtained from atomic spectra; see ref 10.

Chart 4



values were substantially smaller than their experimental values, measured in solution. In fact, this parametrization accounted well for the gas-phase properties: for instance, the calculated λ for 1 was in agreement with the experimental UV spectrum of this compound in the gas phase,[19] and likewise the calculated β was similar to that obtained by Teng and Garito for gas-phase CNDO/S calculations.[20]

In method B, which had been applied previously by Morley et al.[11,21] to large sized molecules, C_{AA} and κ_p are optimized independently in order to match the UV spectra and ground state dipole moments of the molecule in nonpolar solvents. For compounds 1-X, the optimized parameters that we adopted (Table 1) were in fact similar to those given by Morley. This parametrization method yielded excited state energies and first hyperpolarizability values in good agreement with experiments (Table 2). As usually observed in CNDO calculation, the ground state dipole moments μ were *ca.* 20% overestimated with respect to the experimental data for these molecules.

The advantage of using this parametrization method has been recently discussed by Morley, who suggested that the variation of Γ_{AA} which comes out from eq II-4 might be physically interpreted in terms of the effect on an internal dielectric constant.[22] This method proved also suitable for the calculation of molecules containing sulfur. In this case, we introduced an additional constant (κ_d),[23] in order to take into account the 3d orbitals of sulfur, and the Slater orbital exponents and bonding parameters $\beta_S{}^0$ were optimized independently (Table 1).

These preliminary calculations celarly revealed the superiority of parametrization method B for the prediction of molecular first-order hyperpolarizabilities in nonpolar solvents; for this reason, all the calculations discussed below were carried out by this method.

III. Vanillin, Isovanillin, and Their Sulfur Derivatives (1–6)

We begin with a discussion of the first-order hyperpolarizability of vanillin and its sulfur derivatives. The geometries used in the calculations were generated by molecular modeling.[24] The RO and RS substituents were set coplanar to the aromatic ring to which they are bound,[25] and the coordinate system was chosen so that the benzene ring and substituents lie in the *xy* plane as shown in Chart 4. For 1–6, two planar conformations, a and b, of the aldehyde group were considered, as these conformations are very close in energy.[26]

Table 3. Calculated and Experimental Lowest Energy Transitions and Ground State Dipole Moments of Vanillin and Thiovanillin Derivatives 1, 3, and 5 and Isovanillin and Isothiovanillin Derivatives 2, 4, and 6[a]

	λ_{exp}	λ_{calcd}	μ_{exp}	μ_{calcd}
1	305	320	3.20	(a) 2.87 (b) 6.53
3	325	342	1.92	(a) 1.53 (b) 6.07
5	326	357	3.20	(a) 2.89 (b) 3.29
2		322		
4		339		
6		316		

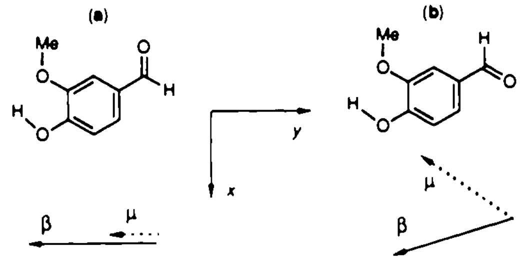
[a] Same units as in Table 1; conformations a and b are shown in Chart 4.

Table 4. Calculated and Experimental Hyperpolarizabilities β (10^{-30} esu) for Vanillin ad Thiovanillin Derivatives 1, 3, and 5 and for the Corresponding Iso Derivatives 2, 4, and 6[a]

	$\beta_{exp}{}^{2\omega}$	$\beta_{vec}{}^{2\omega}$	$\beta_{\mu}{}^{2\omega}$	$\beta_{av}{}^{2\omega}$
1	5.8	12.2	12.2 (a) 7.1 (b)	10.1
3	12.1	22.8	19.9 (a) 7.4 (b)	14.4
5	14.0	32.6	18.9 (a) 19.0 (b)	19.0
2		13.1		
4		14.7		
6		16.6		

[a] See Chart 5 for conformations a and b.

Chart 5



For 1, 3, and 5, both conformations yielded similar computed transitions energies, in good agreement with the experimental UV spectra (Table 3). The calculated dipole moments were different for conformations a and b; the smaller values, close to the measured dipole moments in dioxane, were obtained for conformation a. This result is consistent with the fact that weakly polar solvents favor the least polar conformations of flexible molecules and suggests that in dioxane the conformational equilibrium of the aldehyde functions in 1, 3, and 5 is shifted toward a.

With regard to the hyperpolarizabilities, conformations a and b led to *similar* values of β_{vec} and to *different* values of β_{μ} (Table 4). This phenomenon simply arises from a change in the relative direction of μ (ground state dipole moment) with respect to Δμ (dipole moment difference between the ground state and the first excited charge transfer). For example, in vanillin (Chart 5), μ and Δμ (and then β) are nearly parallel to *y* for conformation a, while these vectors lie on both sides of *y* for conformation b. Assuming that the experimental hyperpolarizability reflects the contributions of a and b, β_{exp} should be compared with β_{av}, obtained from eq III-1 (Boltzmann distribution), in which *E* is the conformational energy of a or b, and β_{μ}, the calculated hyper-

---

(19) Bertinelli, F.; Palmieri, P.; Brilliante, A.; Taliani, C. *Chem. Phys.* **1977**, *25*, 33.

(20) By taking into account solvent effects in the calculation of excited state energies, these authors (ref 17) could reproduce correctly the solution spectra and hyperpolarizabilities.

(21) (a) Docherty, V. J.; Pugh, D.; Morley, J. O. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 1179. (b) Morley, J. O.; Docherty, V. J.; Pugh, D. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1361.

(22) Morley, J. O.; Pavlides, P.; Pugh, D. *Int. J. Quantum Chem.* **1992**, *43*, 7.

(23) Schulte, K. W.; Schweig, A. *Theor. Chim. Acta* **1974**, *33*, 19.

(24) We used either PCMODEL, from Serena Software, P.O. Box 3076, Bloomington, IN 47402-3076, or Hyperchem, from Autodesk, Inc., 2320 Marinship Way, Sausalito, CA 94965-9910.

(25) For a discussion of the conformational preferences of MeO and MeS groups, see ref 2; in the MMX force field used for PCMODEL, and MeS groups are generally calculated to be perpendicular to the benzene ring to which they are bound. This situation does not seem to be realistic, as judged from recent X-ray studies on MeS-substituted cyclotriveratrylenes showing that the MeS substituents are almost coplanar to the benzene rings, like MeO substituents (unpublished work by A. Renault, University of Grenoble). By contrast, the MM+ force field used by Hyperchem yields MeS groups coplanar to the aromatic ring.

(26) For example, in 1, conformations a and b only differ by 0.2 kcal mol^{-1} (MM+ force field).

$$\beta_{av} = \sum_{a,b} \beta_\mu \exp(-E/kT) / \sum_{a,b} \exp(-E/kT) \quad \text{(III-1)}$$

polarizability.[27]

In general, there is an excellent agreement between β_{av} and β_{exp} (Table 4).

The comparison of vanillin (**1**) with its sulfur derivatives **3** and **5** indicates that the thiomethyl and thiol groups are more efficient than the hydroxy group at enhancing β in these compounds. In related works by Singer et al., the enhancement of β caused by sulfur substituents has been considered to mainly involve the excited state properties.[3b] This assumption has been substantiated in the case of (methylthio)benzenes, the first-order hyperpolarizabilities of which are comparable to those of (dimethylamino)benzenes, with a weaker dipole moment and a transparency range significantly shifted toward the UV region.[3a] This feature emphasizes the potential interest of the methylthio group as a donor in the design of molecules for second harmonic generation.

Similar arguments can be raised to interpret the present measurements and calculations on vanillin derivatives, for which there is no apparent relation between the magnitude of the ground state dipole moments and that of β. The weak changes of the dipole moments of **3** and **5** with respect to **1** do not reflect the enhancement of their hyperpolarizability, showing the dominant role of the excited state properties in these molecules. The calculated charges borne by the substituents in vanillin and thiovanillin in the ground and excited states are indicated in Chart 6. In the ground state, the thiol group shows a very weak donor effect compared to the hydroxy group (charges +0.06 and +0.14, respectively); by contrast, the thiol group becomes much more positively charged than the hydroxy group in the lowest excited state (+0.49 and +0.21, respectively). This effect, which probably reflects a larger polarizability of sulfur in the excited state, causes a rotation of the excited state dipole moment and, in turn, a change in the direction of tensor β with respect to μ (a deviation of 25° is calculated for thiovanillin). This phenomenon does not occur for vanillin itself.

The above analysis emphasizes the complementary nature of the information provided by such CNDO/S calculations and by EFISH measurements, for molecules where $\Delta\mu$ and μ are not parallel. In this case, the EFISH method can only provide an approximate value of β, while semiempirical calculations, by supplying all the β_{ijk} components of tensor β, lead to a much better estimate of the actual magnitude of β_{vec}.

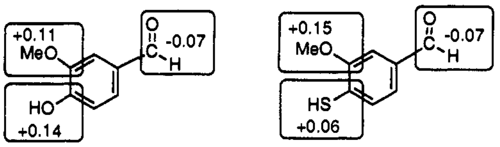
For isovanillin derivatives **2**, **4**, and **6**, only the calculated values of λ, μ, and β are presently available (Tables 3 and 4). Conformations a and b show similar values of β, and the predicted hyperpolarizability of isovanillin (**2**) is of the same order of magnitude as that of vanillin, a result which reflects the comparable donor efficiency of the hydroxy and methoxy groups. In contrast, the sulfur-substituted isoderivatives **4** and **6** show β values markedly lower than those of their regioisomers **3** and **5**, suggesting that the dominant contribution to β originates from the electron-releasing group located *para* to the aldehyde. Thiovanillin rather than isothiovanillin derivatives should therefore be preferred for nonlinear optical applications.

IV. Polyenovanillins

We discuss in this section the hyperpolarizability properties of polyenovanillins **7** for which n = 1–7. The conformations used for these calculations are indicated in Chart 4c,d above. The β_{vec} values that we arrived at are very close for both conformations, but the ground state dipole moments μ differ in magnitude and direction (Table 5). For conformation c, the effect of the length of the conjugation path is illustrated by the variations of β_{vec} versus m, displayed on Figure 2 (m is the number of unsaturated bonds between the donor and acceptor groups, the phenyl ring being counted as equivalent to two ethylenic units; thus $m = n + 2$). The calculations also revealed that, as the number of double bonds increases, the direction of the ground state dipole moment and of that of β tend to become parallel to the polyenic chain (Chart 7).

Chart 6. Charge Distribution in the Ground and Excited States for Vanillin (**1**) and Thiovanillin (**3**)

(I) ground state



(II) first charge-transfer excited state

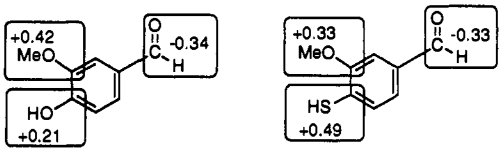


Table 5. Calculated Transition Wavelengths, Dipole Moments, and First-Order Hyperpolarizability Parameters for Conformations c and d of Polyenovanillin Models 7 ($m = n + 2$)

m		λ_{calcd}	μ_{calcd}	$\beta_{vec}{}^0$	$\beta_\mu{}^0$	$\mu\cdot\beta^0$	ρ	V
3	(c)	366	4.26	18.3	18.3	778	114	160
	(d)	383	7.79	18.0	11.5	90		
4	(c)	401	4.35	32.6	32.6	142	173	188
	(d)	404	8.13	31.5	20.1	163		
5	(c)	437	4.74	52.4	52.3	248	214	217
	(d)	439	8.55	50.7	35.7	297		
6	(c)	466	5.25	73.4	73.2	384	299	245
	(d)	467	8.94	72.0	52.8	472		
7	(c)	492	5.45	98.9	98.2	535	363	273
	(d)	493	9.03	96.3	74.1	669		
8	(c)	521	5.47	132.7	132.1	722	441	301
	(d)	522	9.60	129.0	101.4	970		
9	(c)	542	6.07	156.0	155.8	946	474	329
	(d)	541	9.57	153.0	128.9	1233		

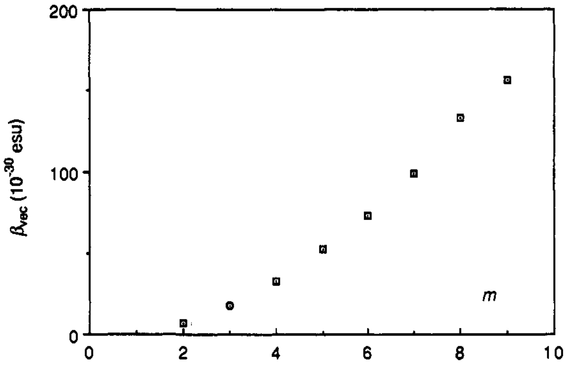


Figure 2. Variation of $\beta_{vec}{}^0$ as a function of the conjugation length in polyenovanillin models **7** ($m = n + 2$).

From a practical point of view, the most interesting parameters to consider here are (i) the $\mu\cdot\beta^0$ product and (ii) the *hyperpolarizability density* ρ ($\rho = \beta^0/V$),[28] which both give information on the existence of a saturation effect.[29]

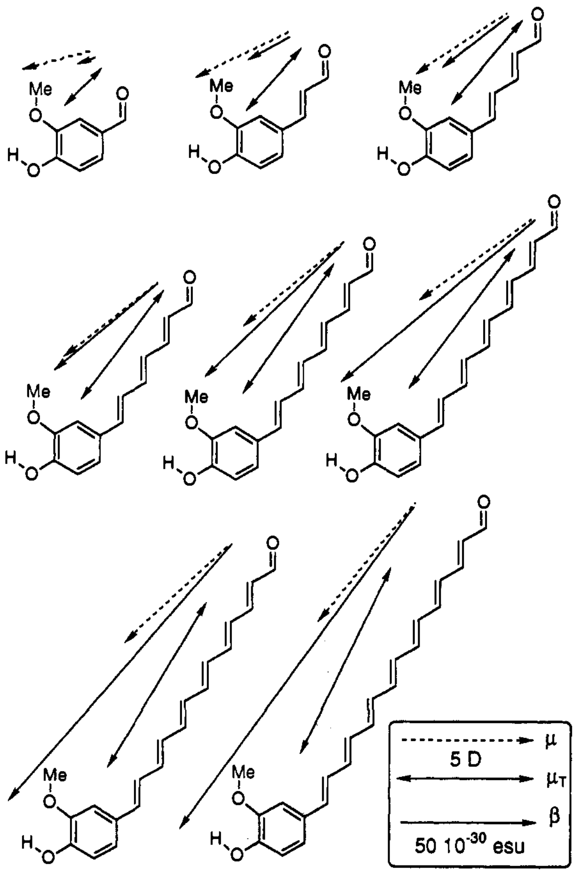
---

[27] Matsuzawa, N.; Dixon, D. A. *Int. J. Quantum Chem.* **1992**, *44*, 497.

[28] The molecular van der Waals volumes V were calculated by using the group increments given by Bondi, see: Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441. Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; Wiley: New York, 1968. Kitaigorodsky, A. I. *Molecular Crystals and Molecules*; Academic Press: London, 1973. Gavezzoti, A. *J. Am. Chem. soc.* **1983**, *105*, 5220.

[29] When the saturation regime is reached, the variation of $\mu\cdot\beta^0$ *vs* m^α is expected to become linear (α = 1), see: Meyers, F.; Bredas, J. L.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 2914.

Chart 7. Magnitude and Orientation of the Vector Part of β (Solid Arrows), the Ground State Dipole Moment μ (Dashed Arrows), and the Transition Dipole of the First Charge Transfer Excitation μ_{CT} (Double Headed Arrows) in Polyenovanillins 7 (n = 0–7)[a]



[a] The directions of the $\Delta\mu$'s (not shown) are almost parallel to the corresponding β's, with a maximum deviation of 7° (for vanillin itself).

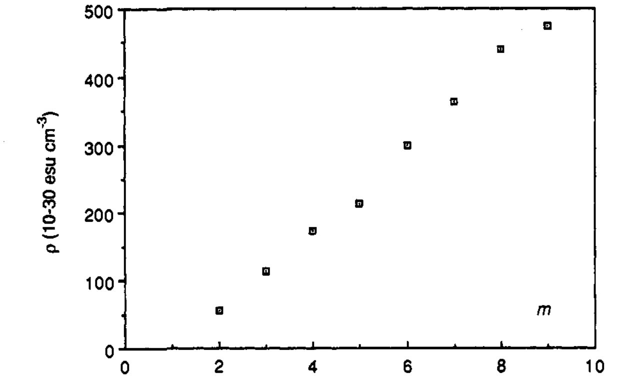


Figure 3. Hyperpolarizability density density ($\rho = \beta^0/V$) as a function of the conjugation length in 7.

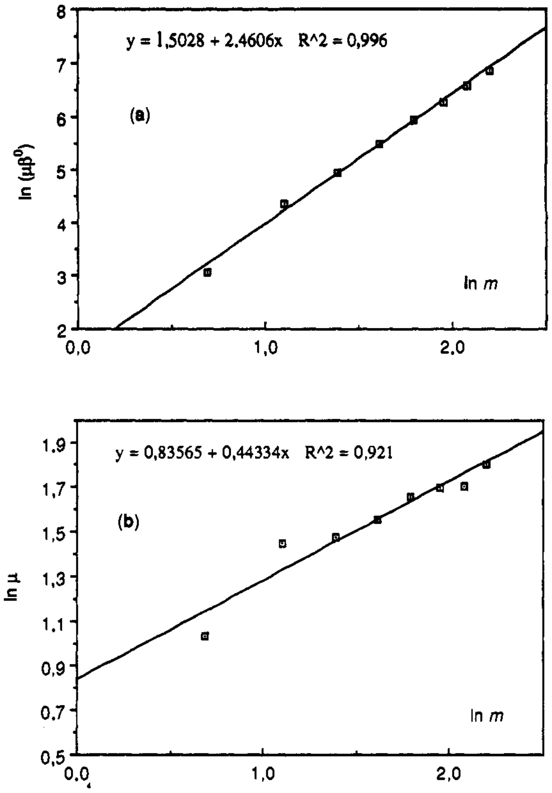


Figure 4. (a) Variation of $\ln(\mu\cdot\beta^0)$ *vs* ln m and (b) variation of ln μ *vs* ln m in 7.

At least up to seven double bonds in the polyenic chains (m = 9), no saturation effect was predicted for the hyperpolarizability density (Figure 3), and the $\mu\cdot\beta^0$ product showed a quasi-quadratic variation (as $m^{2.5}$) against m (Figure 4a). This result is consistent with previous observations or calculations of the variation of $\mu\cdot\beta^0$ as m^α (α = 2.9 or 2.4 in push–pull polyenes,[30] α = 3.0 in α-p-methoxyphenyl-ω-p-nitrophenyl polyenes,[31] and α = 2.1 in α,ω-diphenyl polyene oligomers).[32] Since μ varies as $m^{0.44}$ (Figure 4b), the influence of the chain length on $\mu\cdot\beta^0$ arises from a quadratic dependence of β.

In the two-level model, the component of the β tensor along μ in a static field can be expressed as eq IV-1,[33] where $\lambda = 2\pi c/\omega$

$$\beta^0_{\mu\mu\mu} = \frac{3e^2\lambda^3 f\Delta\mu}{8m\pi^2hc^3} \qquad \text{(IV-1)}$$

is the wavelength of the first charge transfer transition, f its oscillator strength (defined as $f = (2m/e^2\hbar)\omega\mu_{CT}^2$), and $\Delta\mu = \mu_e - \mu_g$ the modulus of the dipole moment difference between the two levels. The validity of this equation is restricted to 1-D systems in which μ, $\Delta\mu$, and μ_{CT} (the transition moment of the first charge transfer excitation) are parallel, a requirement that, as already stated above, is in fact satisfactorily fulfilled in polyenovanillins (see Chart 7).[34]

In our calculations, $\Delta\mu$ was found to remain almost constant as the length of the polyenic chain increased ($\Delta\mu$ varied between 9.2 and 10.3 D for m = 2–9).[35] This feature can be explained in the following way: (i) at the ground state, the dependence of μ_g as $m^{0.44}$ (Figure 4b) indicates that there is only a weak variation (increase) of the extent of charge transfer between donor and acceptor groups, as the conjugation length increases; (ii) the same conclusion holds for the excited state, where the extent of charge transfer (defined as the total charge q_e borne by the CH=O group) increases linearly with $1/m$ (Figure 5), and thus decreases with r, the conjugation length. Since one has roughly $\mu_e = q_e r$, then the excited state dipole moment, as the ground state one, is expected to be almost constant, hence the constancy of $\Delta\mu$. These results are consistent with relevant calculations in other

---

(30) See ref 29 and Barzoukas, M.; Blanchard-Desce, M.; Josse, D.; Lehn, J.-M.; Zyss, J. *Chem. Phys.* **1989**, *133*, 323.

(31) Hujts, R. A.; Hesselink, G. L. J. *Chem. Phys. Lett.* **1989**, *156*, 209.

(32) Dulcic, A.; Flytzanis, C.; Tang, C. L.; Pepin, D.; Fétizon, M.; Hopillard, Y. *J. Chem. Phys.* **1981**, *74*, 1559.

(33) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664.

(34) For a generalized application of the two-level model to 2-D molecules, see: Wortmann, R.; Krämer, P.; Glania, C.; Lebus, S.; Detzer, N. *Chem. Phys.* **1993**, *173*, 99.

(35) The observation that $\Delta\mu$ remains constant or even decreases as the conjugation length increases is not without precedent. For instance, in biphenylpolyenes, $\Delta\mu$ has been found experimentally to decrease as $1/r$, r being the extension of the polyenic chain, see: Shin, D. M.; Whitten, D. G. *J. Phys. Chem.* **1988**, *92*, 2945.

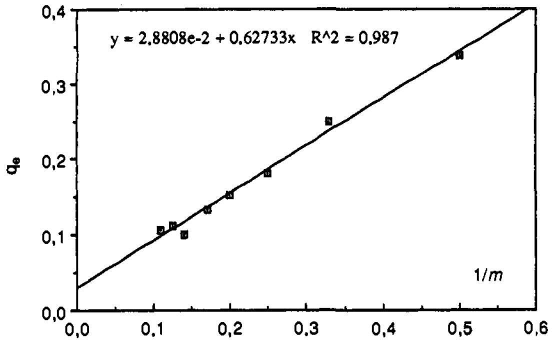


Figure 5. Charge borne by the aldehyde group in the first excited state *vs* $1/m$ in polyenovanillins **7**.

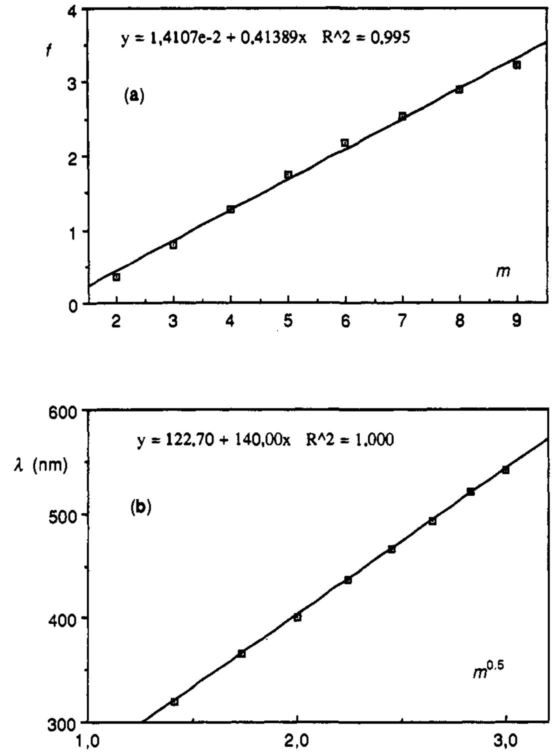


Figure 6. Oscillator strength *f* *vs* *m* (a) and wavelength of the first charge transfer state *vs* $m^{0.5}$ (b) in polyenovanillins **7**.

push–pull polyenes[26,36] and are in agreement with Dulcic model.[37]

By contrast, the oscillator strength *f* of the lowest charge transfer transition increases linearly with *m* (Figure 6a), while the corresponding wavelength λ increases linearly with $m^{0.5}$ (Figure 6b), like in other polyenic systems.[38] Thus, the reason why β increases with the conjugation length in these systems seems to originate primarily from the increase of the oscillator strength[39] and from the red shift of the first electronic transition.

It is interesting to compare the magnitudes of the first-order hyperpolarizabilities of polyenovanillins with those of other polyenes that have already been studied theoretically or experimentally. The data assembled in Table 6, concerning hyperpolarizable molecules having the same conjugation length (n = 3), indicate that the predicted magnitudes of $\beta_\mu{}^0$ in polyenovanillins **XI** and **XII** are at least as large as those of **V** and **VII**, without appreciable red shift of the first electronic transition. It is worth noting that the predicted static hyperpolarizability of the thiovanillin derivative **XII** is of the same order of magnitude as that of the *p*-dimethylamino derivative **VIII**. *Thus, the thiovanillyl group (and its S-alkylated derivatives) can be considered to be equivalent to the p-(dimethyamino)phenyl group in its ability to enhance the hyperpolarizability of push–pull polyenic systems.* This circumstance, and the fact that the vanillyl and thiovanillyl groups are chemically more stable and, in general, less prone to side reactions than the (dimethylamino)phenyl group, clearly strengthens the practical interest of such systems.

Table 6. Calculated Transition Wavelengths λ_{calcd} (nm), Hyperpolarizabilities $\beta_\mu{}^0$ (10^{-30} esu), and Ground State Dipole Moments μ (D) for Trienes **V** and **VII** and **trienovanillines XI** and **XII**[a]

	λ_{calcd}	$\beta_\mu{}^0$	μ
V	427	44	6.5
VIII	446	65	8.5
XI	437	52	4.7
XII	451	69	3.3

[a] See structural formulas in Chart 3.

V. Bisvanillin

We finally discuss the effect of the torsion angle on the hyperpolarizability of bisvanillin (**11**). The starting geometry of the biphenyl system was that of the *cisoid* lowest energy conformer, obtained by energy minimization in the MMX force field (Chart 2). If the orientation of the phenolic hydrogens is disregarded, this conformer exhibits an overall C_2 symmetry, with a torsion angle θ of 60°. The conformations used in the CNDO/S calculations were derived from this geometry by rotation around the central bond, without further energy minimization. The torsion angle was allowed to vary from 15° (*cisoid* conformation) to 180° (*transoid* conformation, see Chart 2). No calculation was effected for $\theta < 15°$, owing to the severe interaction occurring between the OH substituents in this case.

For all the torsion angles considered, the calculations accounted correctly for the C_2 symmetry of the molecule. In all cases, the computed ground and excited state dipole moments and β_{vec} were aligned with the 2-fold axis, as would be expected from simple symmetry arguments. The following comments seem relevant: (i) the ground and excited state dipole moments of the dimer were essentially equal to the vector addition of the dipole moments of the monomer units; (ii) for conformations having $\theta < 120°$, the magnitude of β_{vec} in the dimer was greater than that in the monomer; (iii) for θ smaller than 40°, β_{vec} was *larger* than the vector addition of the contributions of the vanillin monomers (Figure 7).[40] These observations can been interpreted by considering that the hyperpolarizability of bisvanillin has two components, (i) β_{mon}, which represents the contribution of each vanillin monomer, and (ii) β_{CT}, which is related to the extent of intramolecular charge transfer between these fragments. Thus, $\beta = \beta_{mon} + \beta_{CT}$.[41] For θ larger than 40°, β is calculated to be almost exactly the vector addition of the contributions of each of the monomer units, which are then totally decoupled from one another; in that case, there is no appreciable charge transfer between the two benzene rings and thus no β_{CT} contribution; on the contrary, for smaller values of θ, the magnitude of β is *larger* than the vector addition of the vanillin monomers, indicating

---

[36] Brédas, J. L.; Meyers, F. *Nonlinear Opt.* **1991**, *1*, 119.

[37] This model predicts a $1/r$ dependence of the amount of charge transfer q (r being the distance between the ends of the bisubstituted conjugated system bearing charges $-q$ and $+q$). See ref 32.

[38] Jaffé, H. H.; Orchin, M. *Theory and Application of Ultraviolet Spectroscopy*; John Wiley and Sons: New York, 1962; pp 228–41 and references therein. In diphenylpolyenes, the absorption wavelength has been found to be a linear function of $n^{0.5}$.

[39] For a relevant discussion of this point, see: Gao, X. L.; Feng, J. K.; Sun, C. C. *Int. J. Quantum Chem.* **1992**, *42*, 1747.

[40] Similar results have been reported for cyanobiphenyl-based liquid crystals: Risser, S. M.; Ferris, K. F. *Nonlinear Opt.* **1991**, *1*, 195.

[41] The first-order hyperpolarizability of push–pull molecules is often considered to arise from two contributions, β_{add}, which represents the sum of the contributions of the donor and acceptor, and β_{CT}, which accounts for the extent of charge transfer between these groups ($\beta = \beta_{add} + \beta_{CT}$); for instance, see ref 33. In bisvanillin, the same type of argument should be modified by considering that $\beta_{mon} = (\beta_{add} + \beta_{CT})_{mon}$ and $\beta_{dim} = \beta_{mon} + (\beta_{CT})_{dim}$ where $(\beta_{CT})_{dim}$ now represents the charge transfer occurring between the two identical vanillin units when they are conjugated.

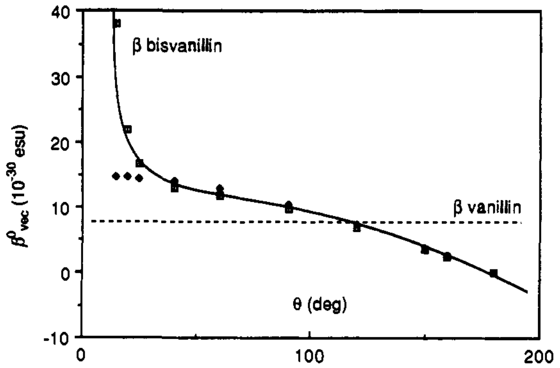


Figure 7. First-order hyperpolarizability $\beta_{vec}{}^0$ of bisvanillin (**11**) as a functio nof the torsion angle θ (solid line); the black dots present the vector addition of the monomers $\beta_{vec}{}^0$, the magnitude of which is indicated by the dotted line.

that there must be some π-electron exchange between the two rings due to conjugation. For instance, at $\theta = 15°$, the calculated β (38×10^{-30} esu) is 2.5 times larger than the vector addition of the monomer contributions (14.7×10^{-30} esu). On going from 90° to small values of θ, there is a red shift of the lowest energy transition from 319 to 494 nm, in relation to the conjugation. Such information suggests that small torsion angles in the *cisoid* conformation would give the best results in terms of hyperpolarizability. This conclusion is in line with recent theoretical calculations and experimental measurements of the first and second hyperpolarizabilities in *unsymmetrical* bi- and polyaryl systems, for which similar effects of the twist angle between the aromatic units have been evidenced.[40,42]

VI. Conclusion

The aim of this work was to set up a theoretical tool allowing us to understand and predict the first-order hyperpolarizability β of vanillin, polyenovanillin, and bisvanillin derivatives. To this end, we have developed a CNDO/S based program allowing the calculation the β tensor components in large polyenic molecules containing Ar–SH or Ar–SR substituents. This program, using the parametrization technique of François et al.,[10] predicted correctly the transition energies and the magnitude of β in solution for most of the compounds studied. These calculations were particularly relevant, not only in yielding the absolute magnitude of β but also in providing its component along the direction of the ground state dipole moment, allowing a direct correlation to be made between calculations and EFISH measurements.

Among the vanillin derivatives, thiovanillin, where the sulfur group is *para* to the aldehyde function, showed the largest first-order hyperpolarizability, and the better donor efficiency of sulfur *vs* oxygen was clearly evidenced to arise from the excited state rather than from the ground state properties.

In polyenovanillins, the magnitude of β was predicted to increase as m^2 (m being the number of unsaturations between the donor and acceptor groups), without saturation of the hyperpolarizability density at least up to $m = 9$. The increase of β with the length of the conjugation path in these molecules was related to the enhancement of the oscillator strength and to the red shift of the first electronic transition, rather than to an increase of the charge transfer between the donor and acceptor. In fact, the dipole moment difference between the ground and excited state remains almost constant when the conjugation length increases. By comparison with analogous systems, the thiovanillyl group, as the donor, can be considered to the equivalent to the well-known *p*-(dimethylamino)phenyl group, with regard to its ability to enhance β in push–pull polyenes. This finding may have important consequences as the thiovanillyl group is readily available and certainly more stable chemically than is the (dimethylamino)-phenyl group.

In bisvanillin, the magnitude of β is calculated to be the vector addition of the contribution of the two monomer units, except for small torsion angles (smaller than 40° in the *cisoid* conformation), where a significant enhancement due to conjugation is evidenced.

This work, together with recent studies[27] on different systems, confirms that relatively simple semiempirical quantum methods (CNDO, INDO, etc.) can provide accurate information on the electronic properties of large hyperpolarizable molecules and, hence, can aid the design of new molecular materials for which large hyperpolarizabilities are required.

Acknowledgment. We are grateful to M. Rajzmann (Marseille) for useful discussions.

Appendix

EFISH Measurements.[43] These measurements were performed in solution using the wedged cell technique. Each compound was tested in dioxane solution at several concentrations, decreasing from 10^{-1} to 10^{-3} M. The temperature of the solution was controlled throughout the experiments. The fundamental frequency was provided by a Q-switched YAG:Nd laser operating at 1.06 μm at a repetition rate of 80 Hz. The vertical beam polarization was obtained by means of a Glan polarizer. The dc high-voltage pulses (up to 50 kV/cm) were applied synchronously with the optical pulses. The second harmonic, separated from the fundamental harmonic by a set of appropriate filters, was detected by a 56TVP photomultiplier. For each translation of the cell, the signal was averaged 32 or 64 times by an IEEE interfaced digitizer (7912AD-Tektronix). The cell translation was driven by a computer which was also used for data acquisition and processing. Each experiment was calibrated relative to a wedged quartz having the same geometry as the liquid cell; we used the value of 1.2×10^{-9} esu for the quadratic susceptibility of quartz.[44] Least square fit of the concentration dependence of the second harmonic intensity, normalized to the second harmonic intensity of the quartz reference, provided the magnitude of the macroscopic coefficient Γ_0. At such low concentrations, the interactions between the molecules of the substrate could be neglected, and the magnitude of the molecular hyperpolarizability γ was calculated from Γ_0 after substracting the contribution of the solvent. The quadratic hyperpolarizability coefficient β was finally calculated from eq A-1,[45,46] where the molecular dipole moment μ is obtained from eq A-2 according to Onsager.[47]

$$\gamma = \gamma_e + \frac{\beta_{exp}{}^{2\omega}\mu}{5kT} \qquad \text{(A-1)}$$

$$\mu^2 = \frac{9kT}{4\pi N}\frac{(\epsilon_0 - \epsilon_\infty)(2\epsilon_0 + \epsilon_\infty)}{\epsilon_0(\epsilon_\infty + 2)^2} \qquad \text{(A-2)}$$

Theoretical Expression of the First-Order Hyperpolarizability. We assume that the theoretical molecular polarization $p_I{}^{\omega_\sigma}$ at $\omega_\sigma = \omega_1 + \omega_2$ can be deduced from the perturbation theory[12] for frequency mixing, in which the applied field is $\vec{E}(t) = \sum_{f=1}^{2}\vec{E}^{\omega_f}$

---

(42) Kodaka, M.; Fukaya, T.; Yonemoto, K.; Shibuya, I. *J. Chem. Soc., Chem. Commun.* **1990**, 1096. Puccetti, G.; Ledoux, I.; Zyss, J.; Jutand, A.; Amatore, C. *Chem. Phys.* **1992**, *160*, 467.

(43) (a) Singer, K. D.; Garito, A. F. *J. Chem. Phys.* **1981**, *75*, 3572. (b) Levine, B. F.; Bethea, C. G. *J. Chem. Phys.* **1975**, *63*, 2666.

(44) Choy, M. M.; Byer, R. L. *Phys. Rev. B* **1976**, *14*, 1693.

(45) Hauchecorne, G.; Kerhervé, F.; Mayer, G. *J. Phys.* **1971**, *32*, 47.

(46) In general, the electronic term γ_e is neglected in conjugated molecules, as it has been shown experimentally that $\gamma_e/(\beta_\mu/5kT) < 0.1$, see: Singer, K. D.; Sohn, J. E.; King, L. A.; Gordon, H. M.; Katz, H. E.; Dirk, C. W. *J. Opt. Soc. Am. B* **1989**, *6*, 1339.

(47) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486.

$\sin(\omega_f t)$. Accordingly, the polarization at 2ω can be expressed as (A-3), where the applied field is $\vec{E}(t) = 2\vec{E}^{\omega}\sin(\omega t)$. The polarization $p_i^{2\omega}$ in the same applied field $\vec{E}(t)$ can also be written as (A-4), where β_{ijk} represents the first-order hyperpolarizability tensor of the molecule.

$$p_i^{2\omega} = -\left(\frac{e^3}{4\hbar^2}\right)\sum_{n'\neq g}\sum_{n\neq g}(r_{gn'}^{i}r_{n'n}^{k}r_{ng}^{j} + r_{gn'}^{i}r_{n'n}^{j}r_{ng}^{k})\left(\frac{1}{(\omega_{n'}+2\omega)(\omega_n+\omega)} + \frac{1}{(\omega_{n'}-2\omega)(\omega_n-\omega)}\right) + (r_{gn'}^{j}r_{n'n}^{k}r_{ng}^{i} + r_{gn'}^{k}r_{n'n}^{j}r_{ng}^{i})\left(\frac{1}{(\omega_{n'}-\omega)(\omega_n-2\omega)} + \frac{1}{(\omega_{n'}+\omega)(\omega_n+2\omega)}\right) + (r_{gn'}^{k}r_{n'n}^{i}r_{ng}^{j} + r_{gn'}^{j}r_{n'n}^{i}r_{ng}^{k})\left(\frac{1}{(\omega_{n'}-\omega)(\omega_n+\omega)} + \frac{1}{(\omega_{n'}+\omega)(\omega_n-\omega)}\right)E_j^{\omega}E_k^{\omega}\cos(2\omega t) \qquad \text{(A-3)}$$

$$p_i^{2\omega} = 2\beta_{ijk}E_j^{\omega}E_k^{\omega}\cos(2\omega t) \qquad \text{(A-4)}$$

The combination of (A-3) and (A-4) leads to (A-5), which provides a theoretical expression of β_{ijk} and then of β_μ (see eq II-3) that is itself directly comparable to the experimental β_{exp} obtained by EFISH measurements.[48]

$$\beta_{ijk} = -\left(\frac{e^3}{8\hbar^2}\right)\sum_{n'\neq g}\sum_{n\neq g}(r_{gn'}^{i}r_{n'n}^{k}r_{ng}^{j} + r_{gn'}^{i}r_{n'n}^{j}r_{ng}^{k})\left(\frac{1}{(\omega_{n'}+2\omega)(\omega_n+\omega)} + \frac{1}{(\omega_{n'}-2\omega)(\omega_n-\omega)}\right) + (r_{gn'}^{j}r_{n'n}^{k}r_{ng}^{i} + r_{gn'}^{k}r_{n'n}^{j}r_{ng}^{i})\left(\frac{1}{(\omega_{n'}-\omega)(\omega_n-2\omega)} + \frac{1}{(\omega_{n'}+\omega)(\omega_n+2\omega)}\right) + (r_{gn'}^{k}r_{n'n}^{i}r_{ng}^{j} + r_{gn'}^{j}r_{n'n}^{i}r_{ng}^{k})\left(\frac{1}{(\omega_{n'}-\omega)(\omega_n+\omega)} + \frac{1}{(\omega_{n'}+\omega)(\omega_n-\omega)}\right) \qquad \text{(A-5)}$$

---

(48) As was recently pointed out by Burland et al., the sum-over-state method has the advantage that "it yields a frequency-dependent value for the hyperpolarizability directly. Thus one can compare experimental and theoretical results": Burland, D. M.; Walsh, C. A.; Kajzar, F.; Seutein, C. *J. Opt. Soc. Am. B* **1991**, *8*, 2269. For a discussion of problems in the comparison of theoretical and experimental hyperpolarizabilities, see: Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590. For recent applications of this method similar to ours, see for instance: Barzoukas, M.; Josse, D.; Fremaux, P.; Zyss, J.; Nicoud, J. F.; Morley, J. O. *J. Opt. Soc. Am. B* **1987**, *4*, 977. Dehu, C.; Meyers, F.; Brédas, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 6198.