

**Ab initio HARTREE-FOCK INVESTIGATION OF  $\pi$ -CONJUGATED COMPOUNDS PRESENTING LARGE  $\beta^v/\beta^e$  RATIO: MEROCYANINES**

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*Professor Rudolf Zahradník, one of the greatest scientists of chemical physics in the general sense, led efficiently Czech science during very difficult decades. One of us (J. M. A.) benefited personally from his highly stimulating and inspiring seminars and lectures and he was always of the greatest help in his scientific career. It is with great respect, admiration and pleasure that we dedicate this paper to Professor Rudolf Zahradník for his 70th birthday.*

CHF/6-311G\* calculations of the first electronic and vibrational hyperpolarizabilities reveal that merocyanines present a substantial  $\beta^v/\beta^e$  ratio under their quinonoid nonpolar form. It originates from a large vibrational first hyperpolarizability whereas its electronic counterpart is small for this class of push-pull  $\pi$ -conjugated molecules. The transition from the quinonoid to the aromatic configuration is accompanied by an increase of  $\beta^e$  and a decrease of the  $\beta^v/\beta^e$  ratio as well as by a  $\approx 180^\circ$  rotation in the plane of the molecule of  $\beta^e$  and  $\beta^v$  with respect to the molecular frame. Our results support the recent experimental discovery that antiparallel aggregation of aromatic and quinonoid forms of merocyanine is energetically favoured and that their first hyperpolarizabilities, which combine constructively, present both electronic and non purely electronic origins.

**Key words:** *Ab initio* coupled Hartree-Fock; Electronic and vibrational first hyperpolarizabilities; Merocyanines; *Ab initio* calculations.

Quantum chemical evaluations of the first hyperpolarizability ( $\beta$ ) of  $\pi$ -conjugated systems for designing new compounds for nonlinear optical (NLO) applications have up to now exclusively focused on the electronic component ( $\beta^e$ ) and have nearly forgotten

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that the vibrational contribution ( $\beta^v$ ) could be optimized to maximize the total response<sup>1</sup> ( $\beta^e + \beta^v$ ). This has to be related to the nearly vanishing  $\beta^v$  contribution for the second harmonic generation (SHG) phenomena. Recently, particular attention has been given to the vibrational contributions and, since they turn out to be in the static limit of the same order of magnitude as their electronic counterpart, to their optimization<sup>2</sup>.

A few studies have already considered the possible relationships between the electronic and vibrational static first hyperpolarizabilities [ $\beta^e(0;0,0) = \beta^e(0)$  and  $\beta^v(0;0,0) = \beta^v(0)$ ] of push–pull  $\pi$ -conjugated compounds<sup>2–15</sup>. Zerbi and coworkers<sup>3–5</sup> have found that, for many second-order NLO conjugated molecules ranging from push–pull substituted benzenes and stilbenes to polyenovanillins and other substituted polyenes, the calculated electronic and vibrational static hyperpolarizabilities are very similar. Their experimental measurements have confirmed the fact that  $\beta^v(0)/\beta^e(0)$  is close to unity. In the latter case, the vibrational first hyperpolarizability is evaluated from infrared and Raman absorption spectra whereas electric field-induced SHG (ESHG) measurements provide the electronic counterpart which – to be correct – would have required to be extrapolated to zero frequency. This has led them to argue that such a coincidence is not fortuitous and that  $\beta^v$  and  $\beta^e$  are just two manifestations of the same underlying physical phenomenon; the connection being the strong electron-phonon coupling along the coordinate associated with the variation of the bond length alternation (BLA).

Using the two-state approximation for describing the electronic properties and  $\beta^e(0)$  whereas the vibrational motions and  $\beta^v(0)$  are evaluated at the doubly harmonic oscillator approximation by neglecting all the modes but the BLA mode, Castiglioni *et al.*<sup>6</sup> have managed to demonstrate their assumption, *i.e.*  $\beta^v(0)$  and  $\beta^e(0)$  are equivalent. However, their approach neglects one of the two terms<sup>7,8</sup> that could dominate the  $\beta^v(0)$  response.

Kim *et al.*<sup>9</sup> have adopted the valence-bond (VB) charge-transfer (CT) model to determine the variation of the  $\beta^v(0)/\beta^e(0)$  ratio as a function of electronic characteristics of the push–pull compounds. Contrary to Zerbi and coworkers, this simple model leads to a  $\beta^v(0)/\beta^e(0)$  ratio that depends upon the nature of the system. Indeed, for the component of the  $\beta$  tensor along the charge-transfer axis, they obtained in the static limit that

$$\beta^v(0)/\beta^e(0) = [6t^2k(Q_{\text{CT}} - Q_{\text{VB}})^2/\Delta^3] , \quad (I)$$

where  $t = \langle \text{VB}|H|\text{CT} \rangle$  is the transfer integral,  $k$  the force constant associated with the BLA mode,  $\Delta$  the energy gap and  $Q_{\text{CT}} - Q_{\text{VB}}$  is the change of BLA normal coordinate between the equilibrium geometries of the CT and VB states, respectively. Nevertheless, their study shows that despite of Eq. (I) the  $\beta^v(0)$  and  $\beta^e(0)$  display a very close behaviour as a function of the BLA. In addition, careful analysis of the assumptions made in the VB–CT model has revealed that simple relations between electronic and

vibrational static properties can be derived<sup>14</sup>. However, these ideal relations, for instance  $[(\beta^v/\alpha^v)/(\beta^e/\alpha^e)] = 3$ , have not been reproduced by *ab initio* CHF/6-31G calculations on a series of reference compounds<sup>14</sup>.

Painelli<sup>10</sup> has recently proposed a similar analysis of the importance of the static  $\beta^v$  contribution by adopting the VB–CT model and has showed that  $\beta^v$  is proportional to the polaron binding energy, a measure of the strength of the electron–phonon coupling. Her study has also the merit to explain why the relation of Castiglioni *et al.*<sup>6</sup> is often qualitatively correct even if one important term is missing<sup>7</sup>.

The ideal equivalence relation of Zerbi *et al.* is further questionable on the basis of the results of two recent studies. On one hand, the  $\beta^v(0)/\beta^e(0)$  ratio has been shown to depend strongly upon both the chain length and the nature of the linker<sup>2</sup>. For  $\text{NO}_2/\text{NH}_2$  substituted polyenes, the RHF/6-31G  $\beta^v(0)/\beta^e(0)$  ratio ranges between 2.2 and 1.7 for polyene chains containing 2 to 8 double bonds whereas for polyyne-based linkers, the ratio is closer to unity and for thiophene-based linkers, the ratio is close to 3. Moreover, *p*-doping the  $\text{NO}_2-(\text{CH}=\text{CH})_n-\text{NH}_2$  compounds strongly alters the BLA pattern and leads to a decrease of the  $\beta^v(0)/\beta^e(0)$  ratio in such a way it ranges between 0.57 at  $n = 2$  and 0.63 at  $n = 8$ . On the other hand for a set of monosubstituted benzenes, both the inductive and mesomeric effects should be considered to account for the variations in  $\beta^v(0)$  upon substitution whereas for  $\beta^e(0)$ , the mesomeric effects reproduce most of the variations<sup>12</sup>. Other very recent investigations show also that the  $\beta^v/\beta^e$  ratio depends upon the nature of the substituents, size and nature of the conjugated linkers<sup>13–15</sup>.

While addressing the magnitude of the  $\beta^v/\beta^e$  ratio it should always be kept in mind their much different dependences upon the NLO process and the frequency. Indeed,  $\beta^e$  evolves as the square of the frequencies whereas at optical frequencies,  $\beta^v$  is rather nonsensitive to the frequency but depends upon the NLO process.

Although it becomes more and more acceptable that the  $\beta^v/\beta^e$  ratio depends upon the nature of the compounds and therefore that both  $\beta^v$  and  $\beta^e$  should be optimized, for most of the compounds investigated up to now, the  $\beta^v(0)/\beta^e(0)$  ratio remains around unity, *i.e.* it goes from 0.5 to 3.0. It is therefore of particular interest to define geometrical and electronic parameters which could substantially tune it. One way of doing it consists in analyzing compounds with very large  $\beta^v(0)/\beta^e(0)$  ratio and in highlighting the key parameters.

We show in this work that  $\beta^v(0)$  can be one order of magnitude larger than  $\beta^e(0)$ . The next section briefly summarizes the methodological context of our first hyperpolarizability calculations and also addresses the main computational points. The results and discussion relating  $\beta^v(0)$  and  $\beta^e(0)$  to other electronic properties are presented next, and the last section further discusses our values in view of recent experimental results.

## METHODOLOGICAL AND COMPUTATIONAL ASPECTS

The first hyperpolarizability ( $\beta$ ) is the second-order response of the dipole moment with respect to the external electric fields:

$$\begin{aligned}\mu_\zeta(\omega_\sigma) = \mu_\zeta^0 + \sum \alpha_{\zeta\eta}(-\omega_\sigma; \omega_1) E_\eta(\omega_1) + \\ + \frac{1}{2} K^{(2)} \sum_{\eta\xi}^{\eta\xi} \beta_{\zeta\eta\xi}(-\omega_\sigma; \omega_1, \omega_2) E_\eta(\omega_1) E_\xi(\omega_2) + \dots ,\end{aligned}\quad (2)$$

where  $\omega_\sigma = \sum_i \omega_i$  and the summations are running over the field indices  $\eta$  and  $\xi$ , associated to the Cartesian coordinates.  $K^{(2)}$  is such that the  $\beta$  of different NLO processes converge towards the same static value.

When addressing the effects of external electric fields on matter, it is common to resort to the clamped nucleus or canonical (CN) approximation which assumes that the fields act sequentially on the electronic and nuclear motions<sup>16,17</sup>. Adopting the CN scheme leads therefore to the distinction between the electronic including the zero-point vibrational average (ZPVA) and a pure vibrational hyperpolarizability contributions. In that approximation, the nuclei are fixed in position, which means that the vibronic states reduce to electronic states and that the vibronic energy denominators become electronic energy denominators. Several approximate schemes to evaluate the SOS/CN electronic and vibrational responses are available. For a question of computational feasibility, our study has been achieved at the Hartree–Fock level. Obviously, the inclusion of electron correlation effects could lead to modifications of both the geometrical structure and electronic properties; the first hyperpolarizability being also function of the geometry. Although the electron correlation could modulate the  $\beta^v/\beta^e$  ratio, the structure–property relationships should remain.

The coupled-perturbed Hartree–Fock/time-dependent Hartree–Fock (CPHF/TDHF) procedures<sup>18</sup> are probably amongst the most common procedures for computing *ab initio* the static/dynamic electronic (hyper)polarizabilities. In this approach, a term representing the interaction between the external static/dynamic electric fields and the molecular dipole is added to the Fock matrix. Its effects upon the density matrix are obtained by expanding the CPHF/TDHF equation as a power series in the field amplitude and by solving it self-consistently order by order. The successive density matrix derivatives are used to evaluate the electronic (hyper)polarizabilities. For the second-order NLO response,

$$\beta_{\zeta\eta\xi}^e(-\omega_\sigma; \omega_1, \omega_2) = -\text{Tr} [\mathbf{m}_\zeta \mathbf{R}^{\eta\xi}(\omega_1, \omega_2)] \quad (3)$$

with  $\mathbf{m}_\zeta$  the  $\zeta$ th Cartesian component of the dipole moment matrix and  $\mathbf{R}^{\eta\xi}(\omega_1, \omega_2)$  the second-order perturbed density matrix of the molecule submitted to electric fields of frequency  $\omega_1$  and  $\omega_2$  along the  $\eta$  and  $\xi$  directions. This procedure self-consistently includes the field-induced electron reorganizational effects through the average Coulomb and Pauli potentials: it is a fully relaxed SCF approach. The expression for  $\alpha_{\xi\eta}^e(-\omega_\sigma; \omega_1)$  is obtained by replacing  $\mathbf{R}^{\eta\xi}(\omega_1, \omega_2)$  by  $\mathbf{R}^\eta(\omega_1)$  in Eq. (3).

At the double harmonic oscillator level of approximation<sup>19–21</sup> the static vibrational first hyperpolarizability tensor elements read

$$\beta_{\xi\eta\xi}^v(-\omega_\sigma; \omega_1, \omega_2) = [\mu\alpha]^{0,0} = \frac{1}{2} \sum_{-\sigma, 1, 2} P_{-\sigma, 1, 2} \sum_a \frac{\left( \frac{\partial \mu_\xi^e}{\partial Q_a} \right)_0 \left( \frac{\partial \alpha_{\eta\xi}^e}{\partial Q_a} \right)_0}{(\omega_a^2 - \omega_\sigma^2)}, \quad (4)$$

where <sup>0,0</sup> indicates that no electrical or mechanical anharmonicity is included,  $\sum_{-\sigma, 1, 2}$  is a summation over the six permutations of the pairs  $(-\omega_\sigma, \zeta)$ ,  $(\omega_1, \eta)$  and  $(\omega_2, \xi)$ .  $Q_a$  is the normal coordinate of the vibrational motion with circular frequency  $\omega_a = 2\pi\nu_a$ , and the subscript 0 indicates the equilibrium nuclear configuration. The expression of the frequency-dependent vibrational linear polarizability,  $\alpha_{\xi\eta}^v(-\omega_\sigma, \omega_1) = [\mu^2]^{0,0}$ , can be obtained from Eq. (4) by replacing the permutation operator  $P_{-\sigma, 1, 2}$  by  $P_{-\sigma, 1}$  and by replacing  $(\partial \alpha_{\eta\xi}^e / \partial Q_a)_0$  by  $(\partial \mu_\eta^e / \partial Q_a)_0$ .

The hyperpolarizabilities  $\beta^e$ ,  $\alpha^v$ ,  $\beta^e$  and  $\beta^v$  calculations have been performed with the GAUSSIAN94 program<sup>22</sup> on the RHF/6-311G\* (ref.<sup>23</sup>) optimized structures. A tight convergence threshold on the residual forces has been adopted to meet a satisfactory accuracy in computing the  $(\partial P / \partial Q_a)_0$  values.

The hyperpolarizabilities  $\beta^e$  and  $\beta^v$  depend in different ways upon the NLO process as well as upon the optical frequencies. This aspect of the  $\beta^v/\beta^e$  ratio is not tackled in detail in this study. However, in order to address qualitatively the range of variation of the  $\beta_{\xi\eta\xi}^v(-\omega_\sigma; \omega_1, \omega_2) / \beta_{\xi\eta\xi}^e(-\omega_\sigma; \omega_1, \omega_2)$  ratio with respect to the static limit it is important to note that the  $\beta^e$  increase with the frequency obeys the relation<sup>24</sup>,

$$\beta_{\xi\eta\xi}^e(-\omega_\sigma; \omega_1, \omega_2) / \beta_{\xi\eta\xi}^e(0) = 1 + A\omega_L^2 + B\omega_L^4 + \dots, \quad (5)$$

where  $\omega_L^2 = \omega_\sigma^2 + \omega_1^2 + \omega_2^2$ . For the diagonal and average quantities,  $A$  and  $B$  are parameters which depend upon the molecule but not upon the NLO process. On the other hand, the frequency-dependence of  $\beta^v$  is highlighted by adopting the enhanced<sup>25</sup> approximation which relies on the fact that the optical frequencies are at least one order of magnitude larger than the vibrational ones. For any diagonal tensor component of  $\beta^v$  such as the longitudinal one, one obtains:

$$\beta_L^v(-\omega; \omega, 0)_{\omega \rightarrow \infty} = \beta_L^v(0; \omega, -\omega)_{\omega \rightarrow \infty} = \frac{1}{3} [\mu \alpha]_{L; \omega=0}^{0,0} \quad (6)$$

$$\beta_L^v(-2\omega; \omega, \omega)_{\omega \rightarrow \infty} = 0 \quad . \quad (7)$$

In other words,  $\beta^v$  decreases with the frequency and, in particular, for SHG  $\beta_L^v$  is negligible whereas for the dc-Pockels (dc-P) and optical rectification (OR) processes, it amounts to 1/3 of the static quantity. Similar relations can also be written for isotropically averaged quantities such as

$$\beta_\eta = \frac{1}{3} \sum_{\zeta} \beta_{\zeta\zeta\eta} + \beta_{\zeta\eta\zeta} + \beta_{\eta\zeta\zeta} \quad (8)$$

and therefore for

$$\beta_{\text{vec}} = \sum_{\eta} (\mu_{\eta} \beta_{\eta} / |\mu|) \quad \text{and} \quad \beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad , \quad (9)$$

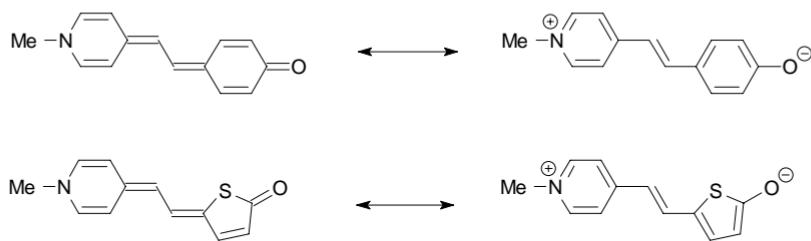
where  $\mu_{\eta}$  and  $|\mu|$  are the components and norm of the dipole moment. This totally different frequency-dependences of the electronic and vibrational phenomena have obviously to be accounted for in optimizing the responses as a function of the NLO process. In what concerns the linear polarizability, the frequency-dependence of the electronic part follows the general form given in Eq. (5) whereas above the vibrational resonances located in the infrared region, the vibrational counterpart decreases rapidly with the frequency and tends towards zero.

## RESULTS AND DISCUSSIONS

The merocyanine dye electronic structure depends upon the nature of the aromatic rings, of the conjugated bridge between these rings, of the eventual substituents, as well as of the environment which all influence the relative stability of its two extreme resonance forms M1 (top) and M2 (bottom) (see Scheme 1).

The nonpolar quinonoid form is favorized by nonpolar solvents whereas polar solvents stabilize the zwitterionic form presenting a larger aromaticity. Numerous studies have highlighted the specificities of their solvatochromism and have been reviewed by Buncel and Rajagopal<sup>26</sup>. For our purpose it is striking to mention that the solvatochromism is associated with substantial SHG- $\beta$  variations<sup>27</sup>. Moreover, the present study will restrictively focus on isolated molecules while keeping in mind that variations of

structure along the quinonoid to aromatic coordinate can be induced by either the solvent or by chemical modifications.



SCHEME 1

The RHF/6-311G\* optimized geometries of the ground state of M1 and M2 show that the quinonoid structure is energetically favored. Figure 1 gives the optimized bond length values (in Å) along the conjugated backbone of M1 and M2.

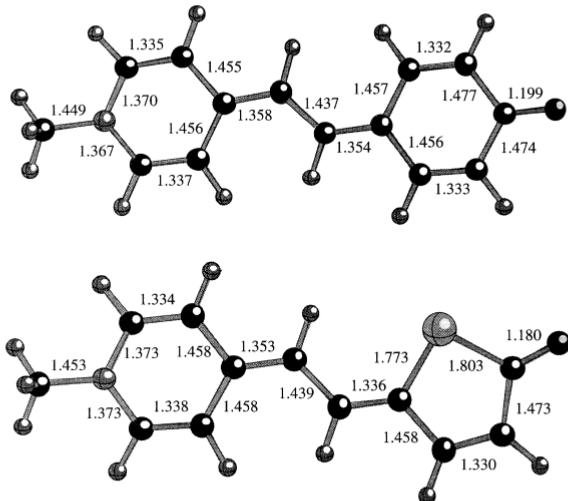


FIG. 1  
RHF/6-311G\* bond length values (in Å) along the conjugated backbone of M1 and M2

$\bar{\alpha}^v(M1)/\bar{\alpha}^v(M2) = 1.16$ ,  $\beta_{vec}^e(M1)/\beta_{vec}^e(M2) = 0.66$  and  $\beta_{vec}^v(M1)/\beta_{vec}^v(M2) = 1.61$  (see Table I). Indeed, neither the BLA nor the charge distribution can explain why  $\beta_{vec}^e(M1)/\beta_{vec}^e(M2) \leq 1.0$ . A possible explanation refers to the smaller aromaticity of the thiophene ring which could therefore undergo a slightly larger aromatic to quinonoid transition, the quinonoid character being associated with a larger  $\beta_{vec}^e$ . On the other hand, it is associated with smaller  $\bar{\alpha}^e$  and  $\beta_{vec}^v$ . The  $\beta_{vec}^v/\beta_{vec}^e$  ratios are important for

TABLE I

RHF/6-311G\* electronic and vibrational contributions to  $\bar{\alpha}(0)$ ,  $\beta_{vec}(0)$  and  $\beta_{tot}(0)$  as well as the  $\beta_{vec}^v(0)/\beta_{vec}^e(0)$  ratios in comparison with the average BLA and the norm of the dipole moment. With the exception of the BLA given in Å, all the values are given in a.u. (1.0 a.u. of dipole moment =  $8.478358 \cdot 10^{-30}$  C m = 2.5415 D; 1.0 a.u. of polarizability =  $1.6488 \cdot 10^{-41}$  C<sup>2</sup> m<sup>2</sup> J<sup>-1</sup> = 0.14818 Å<sup>3</sup>; 1.0 a.u. of first hyperpolarizability =  $3.2063 \cdot 10^{-53}$  C<sup>3</sup> m<sup>3</sup> J<sup>-2</sup> = 8.641  $\cdot 10^{-33}$  esu). For  $MH^+$ , the center of mass has been chosen as the origin of the Cartesian axis.  $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$

Structure	BLA	$ \mu $	$\bar{\alpha}^e$	$\bar{\alpha}^v$	$\beta_{vec}^e$	$\beta_{vec}^v$	$\beta_{vec}^v/\beta_{vec}^e$	$\beta_{tot}^e$	$\beta_{tot}^v$
M1	0.10	5.37	231	65	1 038	22 901	22.1	1 399	22 994
M1H <sup>+</sup>	0.06	4.42	192	75	-9 124	-17 270	1.9	9 208	17 808
M2	0.10	4.46	208	56	1 562	14 255	9.8	2 299	15 160
M2H <sup>+</sup>	0.06	4.29	193	102	-9 940	-26 752	2.7	9 944	26 762
pNA	0.01	2.72	79	27	560	1 419	2.53	572	1 464

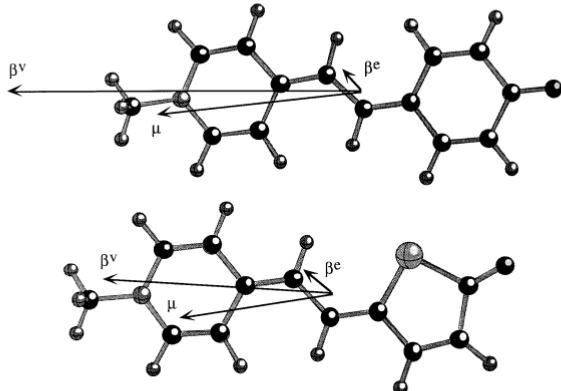


FIG. 2

Orientation of the dipole moment, the electronic and vibrational static first hyperpolarizability vectors with respect to the molecular axis for M1 and M2. The length of the arrow is proportional to the magnitude of the vector

these merocyanines and attain 22.1 and 9.8 for M1 and M2, respectively. If taking pNA as a prototype system, this large  $\beta^v/\beta^e$  ratio is due to both the large  $\beta^v$  value and the rather small  $\beta^e$  value for these extended  $\pi$ -conjugated systems. It is interesting to note that the largest  $\beta^v/\beta^e$  ratio is associated with the largest  $\bar{\alpha}^e$ . For several other compounds, we have found that the largest  $\beta^v/\beta^e$  ratio corresponds to the largest  $\bar{\alpha}^e$  value and, contrary to the merocyanine cases, to the smallest BLA (ref.<sup>13</sup>). Figure 2 represents the relative orientation of both the electronic and vibrational first hyperpolarizability vectors  $\beta = (\beta_x, \beta_y, \beta_z)$  with respect to the molecular axis and the dipole moment. For the two molecules, vectors  $\mu$  and  $\beta^v$  are clearly oriented along the longitudinal axis whereas the much smaller vector  $\beta^e$  is oriented parallel to the bridge C-C bond.

Adding a proton to the oxygen atom favorizes the aromatic form as can be seen from the geometrical parameters given in Fig. 3. The charge distribution is very similar for M1H<sup>+</sup> and M2H<sup>+</sup>: in the order *N*-methyl, pyridine, C<sub>2</sub>H<sub>2</sub> bridge, phenyl (thiophene) and terminal OH, the Mulliken RHF/6-311G\* charges are 0.32 (0.32), 0.47 (0.44), 0.00 (0.06), 0.41 (0.31) and -0.20 (-0.15) for M1H<sup>+</sup> (M2H<sup>+</sup>), respectively. Again, this shows the slightly larger aromatic character of the phenyl species. M1H<sup>+</sup> and M2H<sup>+</sup> present nearly identical  $\bar{\alpha}^e$  and  $\beta_{vec}^e$  whereas M2H<sup>+</sup> has a  $\beta_{vec}^e$  55% larger than M1H<sup>+</sup> (Table I). Since M1H<sup>+</sup> and M2H<sup>+</sup> are charged species, their dipole moment (and therefore  $\beta_{vec}^e$ ) is origin dependent. Consequently, we have chosen the center of mass for the origin and it turns out that in view of their correspondence with  $\beta_{tot}$ , the relations between the  $\beta_{vec}$  quantities do not appear to be biased by this choice. The one-order of magnitude increase of  $\beta^e(0)$  by going from M to MH<sup>+</sup> can be related in first approximation to a BLA decrease or to an increase of electron delocalization along the conjugated path. How-

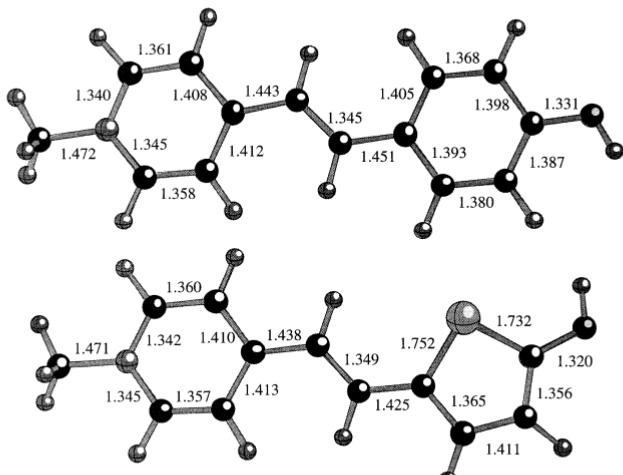


FIG. 3  
RHF/6-311G\* bond length values (in Å) along the conjugated backbone of M1H<sup>+</sup> and M2H<sup>+</sup>

ever, the BLA dependence of  $\beta^v(0)$  is much smaller and goes in the opposite direction for M1/M1H<sup>+</sup>. When going from the neutral to the charged species, the  $\beta^v/\beta^e$  ratios are much smaller as a result of a substantial increase of  $\beta^e$ ; the largest ratio being associated with the most quinonoid system. Comparison of charged and uncharged species points out that protonating M1 decreases the magnitude of  $\beta_{\text{vec}}^v$ , as well as both the  $\bar{\alpha}^e$  and the BLA whereas for M2, the protonation increases  $|\beta_{\text{vec}}^v|$  and decreases both the  $\bar{\alpha}^e$  and BLA values. Altogether, the rationalization of the substantial variations of  $\alpha$  and  $\beta$  in protonated/unprotonated, aromatic/quinonoid, merocyanines seems to be a difficult task for which one-parameter correlation cannot be set up. Nevertheless, in their quinonoid form they present exceptionally large  $\beta^v/\beta^e$  ratios that highlight the importance of  $\beta^v$  in these  $\pi$ -conjugated systems. As drawn in Fig. 4, the addition of a proton changes by roughly 180° the orientation of vectors  $\beta^e$  and  $\beta^v$  with respect to the molecular frame. If choosing the center of mass as the origin of the Cartesian axis, vector  $\mu$  of the charged species remains parallel to the longitudinal axis and pointing towards the CH<sub>3</sub>-N extremity.

An analysis of the most contributing vibrational normal modes reveal that the 1 100–1 800 cm<sup>-1</sup> modes present the largest contributions (Tables II and III). They all involve displace-

TABLE II

RHF/6-311G\* vibrational normal mode frequencies,  $\beta_{\text{vec}}^v(0)$  contributions and relative contributions (given in percent in parentheses) of the most important vibrational normal modes of the M1 and M2 merocyanine dyes. The last lines provide the total electronic and vibrational first hyperpolarizability values

	M1		M2
$\omega$ , cm <sup>-1</sup>	$\beta_{\text{vec}}^v(0)$ , a.u.	$\omega$ , cm <sup>-1</sup>	$\beta_{\text{vec}}^v(0)$ , a.u.
189	1 973 (8.6)	169	850 (6.0)
610	1 105 (4.8)	612	960 (6.7)
1 243	1 618 (7.1)	1 234	582 (4.1)
1 279	1 024 (4.5)	1 246	721 (5.1)
1 288	1 274 (5.6)	1 256	672 (4.7)
1 313	1 376 (6.0)	1 293	1 288 (9.0)
1 718	1 792 (7.8)	1 316	908 (6.4)
1 729	4 358 (19.0)	1 727	2 714 (19.0)
1 743	2 834 (12.4)	1 768	1 729 (12.1)
		1 786	1 786 (17.7)
$\beta_{\text{vec}}^v(0)$	22 9001		14 255
$\beta_{\text{vec}}^e(0)$	1 038		1 562

TABLE III

RHF/6-311G\* vibrational normal mode frequencies,  $\beta_{\text{vec}}^{\text{v}}(0)$  contributions and relative contributions (given in percent in parentheses) of the most important vibrational normal modes of the  $\text{M1H}^+$  and  $\text{M2H}^+$  merocyanine dyes. The last lines provide the total electronic and vibrational first hyperpolarizability values

M1H <sup>+</sup>		M2H <sup>+</sup>	
$\omega$ , cm <sup>-1</sup>	$\beta_{\text{vec}}^{\text{v}}(0)$ , a.u.	$\omega$ , cm <sup>-1</sup>	$\beta_{\text{vec}}^{\text{v}}(0)$ , a.u.
1 254	-2 341 (13.6)	634	-1 032 (3.9)
1 266	-3 941 (22.8)	1 124	-3 723 (12.8)
1 479	-848 (4.9)	1 233	-5 250 (18.0)
1 670	-1 097 (6.3)	1 286	-3 336 (11.4)
1 718	-873 (5.1)	1 426	-2 108 (7.2)
1 737	-2 450 (14.2)	1 578	-4 254 (14.6)
1 769	-632 (3.7)	1 755	-1 315 (4.5)
$\beta_{\text{vec}}^{\text{v}}(0)$	-17 270		-26 752
$\beta_{\text{vec}}^{\text{e}}(0)$	-9 124		-9 940

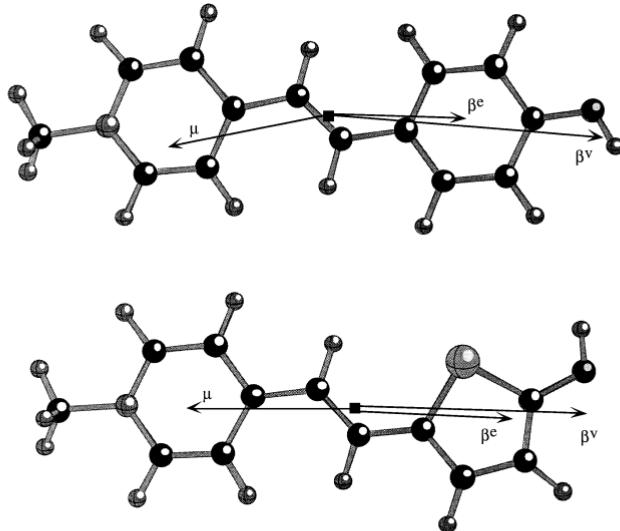


FIG. 4

Orientation of the dipole moment, the electronic and vibrational static first hyperpolarizability vectors with respect to the molecular axis for  $\text{M1H}^+$  and  $\text{M2H}^+$ . The length of the arrow is proportional to the magnitude of the vector. The dipole moment is defined with respect to the center of mass

ments of the backbone atoms (Fig. 5) in a way which affects considerably the BLA and charge transfer along the conjugation direction. Therefore they lead to substantial  $(\partial\alpha_{\eta\xi}^e/\partial Q_a)_0$  and  $(\partial\mu_{\eta}^e/\partial Q_a)_0$  values. These motions are accompanied by hydrogen motions which do not significantly contribute to the  $(\partial P/\partial Q_a)_0$  quantities. Such simple picture of the  $\beta^v$  origin is of importance with respect to the optimization of the vibrational contribution to the NLO properties because, *in fine*, one would be able to tune specifically the geometric and electronic parameters which mostly affect the vibrational contributions of these modes. Moreover, the vibrational frequency is related to the response time: the lower the frequency, the slower the process. For these the 1 100–1 800 cm<sup>-1</sup> modes, the response time is roughly one order of magnitude larger than for the electronic processes associated with electronic transitions of 1–3 eV.

### FURTHER DISCUSSION AND CONCLUSIONS

For several aspect, our *ab initio* characterization is in agreement with the properties of the co-crystal reported by Pan *et al.*<sup>30</sup> where merocyanines and protonated merocyanines are in an antiparallel orientation whereas their first hyperpolarizability vectors are parallel and are constructively reinforced. This ideal chromophoric alignment has been obtained by taking advantage of the specific hydrogen-bonding interactions. In addition, for these co-crystals, Wang *et al.*<sup>31</sup> have reported later that the electronic part of the electro-optic coefficient  $r_{111}^e(-\omega; \omega, 0)$ , calculated by using the measured  $d_{11}(-2\omega; \omega, \omega)$  coefficient (SHG), and correcting with the two-level model for the dispersion effects, is consistently smaller than the measured electro-optic coefficient. This difference indicates the presence of substantial not purely electronic electro-optic effects. From our theoretical investigation, it is possible to estimate an upper bound of 1.32 to the  $\beta_{\text{vec}}^v(-\omega; \omega, 0)/\beta_{\text{vec}}^e(-\omega; \omega, 0)$  ratio for the M1–M1H<sup>+</sup> antiparallel aggregate. This important ratio at optical frequency demonstrates that the vibrational contributions have certainly to be considered to account for the difference between the electro-optic and SHG coefficients measured by Wang *et al.*<sup>31</sup>.

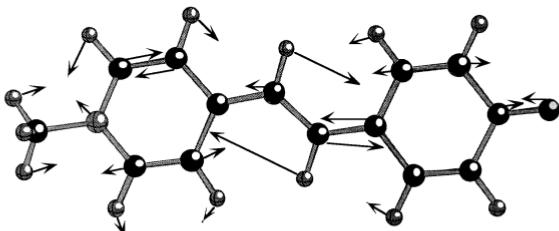


FIG. 5

Schematic representation of the most contributing mode (1 729 cm<sup>-1</sup>) to  $\beta_{\text{vec}}^v(0)$  of M1. The length of the arrows is proportional to the atomic displacements which occur in the molecular plane

In summary, the  $\beta^v$  of merocyanine and protonated merocyanine dyes is substantial. Moreover the neutral molecules which adopt a quinonoid conformation are characterized by very large  $\beta^v/\beta^e$  ratios. No simple relation has been found to rationalize the variations in  $\beta^e$ ,  $\beta^v$ ,  $\alpha^e$  and  $\alpha^v$  with respect to the protonation and the substitution of the phenyl by the thiophene ring. In view of the hydrogen-bonding-driven self-assembled co-crystallization lattice which ideally aligns the chromophores for NLO efficiency<sup>30,31</sup>, it turns necessary to further optimize both the electronic and vibrational hyperpolarizabilities of merocyanine derivatives with respect to chemical modifications as well as to describe the effects of the surrounding upon their linear and nonlinear responses.

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