J. Phys. Chem. A **2008,** *112,* 11861–11872 **11861**

First- and Second-Order Polarizabilities of Simple Merocyanines. An Experimental and Theoretical Reassessment of the Two-Level Model

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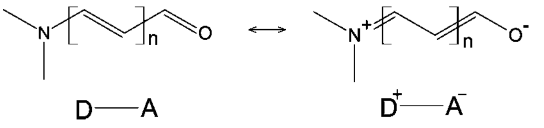
Received: September 11, 2008

Taking four merocyanines [$(CH_3)_2N-(CH{=}CH)_n-C(CH_3)O$; $n = 1-4$] (Mc1−4) as test D−A systems, we performed a close experimental and theoretical examination of the two level model with reference to its ability to provide correct predictions of both absolute values and dependence on the conjugation path length of first- and second-order molecular polarizabilities. By ^{1}H NMR spectroscopy merocyanines Mc1−4 were found to be ~1:1 mixtures of two planar conformers with cis and trans arrangements of the $-C(CH_3)O$ electron-acceptor group and all trans structure of the polyene like fragment. The degree of bond length alternancy (BLA) in the $-(CH{=}CH)_n-$ fragment, was quantified by extensive full geometry optimizations at both semiempirical and ab initio level. DFT (6-31G**/B3LYP) optimized geometries were considered to be most reliable and were used for calculations of the excited-state properties. The applicability of the two level model, reducing the general sum-over-states (SOS) expansion to only one term involving the ground state (g) and the lowest-lying $^1(\pi\pi^*)$ CT state (e), was checked by analysis of fluorescence and near UV absorption spectra. Measurements of the basic two-level model quantities (E_{ge}, μ_{ge} and $\Delta\mu_{eg}$), by which the dominant components of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ tensors are expressed (α_{XX}, β_{XXX}, $X \equiv$ long molecular axis), were designed to give approximate free-molecule values. It is proposed, in particular, an adjustment of the solvatochromic method for the determination of $\Delta\mu_{eg}$, based on accurate measurements of absorption spectral shifts in *n*-hexane/diethyl ether mixtures with small diethyl ether volume fractions. Such an approach led to Mc1−4 β_{XXX}'s matching well in both value and *n*-dependence with EFISH data reported in the literature for similar merocyanines. For the fluorescent Mc4, the results were qualitatively well reproduced by an approach, which combines absorption and fluorescence solvent shifts. All the measured quantities were calculated for both trans and cis Mc1−4 by three semiempirical INDO-based approaches aiming at evaluating the performances of different integral parametrizations and CI extensions: ZINDO/S, CS INDO SCI, CS INDO SDCI. In all cases, α_{XX} and β_{XXX} were found to rise proportionally to about $n^{1.3}$ and n^2, respectively, in qualitatively good agreement with the experimental values. As to the absolute values, however, experimental α_{XX}'s and β_{XXX}'s were best reproduced by CS INDO SDCI combining Ohno−Klopman parametrization and CI including both single and double excitations. The validity of the two-level model was checked by comparison with converged SOS calculations for the longest chain merocyanine (Mc4) and finite field calculations of linear polarizabilities for all of the four dyes (Mc1−4).

1. Introduction

CHART 1



The search for molecules characterized by large hyperpolarizabilities is a necessary step in the optimization of molecule-based materials for nonlinear optical (NLO) applications.[1,2] Much of the extensive theoretical and experimental work published on this subject has focused on the design of molecular architectures capable of enhancing the first hyperpolarizability β. Nowadays, it is well established that the best candidates for high β are the so-called donor−π−acceptor, or simply D−A, systems including push−pull substituted benzenes, stilbenes, polyphenyls, polyenes, polyynes, etc. (see refs 3 and 4 for surveys of the pertinent literature). Of great interest, among the many types of D−A systems, are the merocyanines whose primary chromophores (streptomerocyanines) can be schematized by the formula $D-(CH{=}CH)_n-A$, where $D = NR_2$ and $A = CHO$. In recent years, we have investigated, both theoretically and experimentally, the photochemical and spectroscopic properties of merocyanines with reference to their peculiar electronic structure, describable in terms of a neutral and a charge-separated mesomeric form (Chart 1), and the role of the solvent.[5,6] By treatment of the solute−solvent interactions at the SCF CS INDO level, in ref 6 we were able to provide qualitatively good descriptions of solvent influence on absorption and fluorescence spectra of both positively and negatively solvatochromic merocyanine dyes. In terms of the Onsager dipolar model, the strong solvatochromism exhibited by many merocyanines is related to an appreciable change in dipole moment ($\Delta\mu_{eg} = \mu_e - \mu_g$) associated with the charge-transfer (CT) transition from the ground state (g) to the first $^1(\pi\pi^*)$ (essentially HOMO−LUMO) state (e).[7,8] This very phenomenon, traceable to a marked excitation-induced change in the contribution of the charge-separated resonance form, is known to determine the high first hyperpolarizabilities of these com-

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10.1021/jp8080854 CCC: $40.75

pounds according to the simple "two-level" model,[9] which relates the dominant component of the static third-rank tensor $\boldsymbol{\beta}$, interpreted as the vector projection of β along the CT direction, to $\Delta\mu_{eg}$ by the expression

$$\beta_{CT} \propto \Delta\mu_{eg} \frac{\mu_{ge}^{2}}{E_{ge}^{2}} \qquad (1)$$

where μ_{ge} and E_{ge} are the dipole matrix element and the energy of the g → e transition, respectively. Within this model the dominant component of the static second-rank polarizability tensor $\boldsymbol{\alpha}$ is simply given as

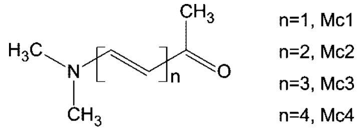
$$\alpha_{CT} \propto \frac{\mu_{ge}^{2}}{E_{ge}} \qquad (2)$$

Comprehensive theoretical studies of linear polarizabilitiy α and first and second hyperpolarizabilities, β and γ, were published several years ago for some classic merocyanine dyes.[10,11] References 10 and 11 laid stress on the dependence of the NLO properties on the degree of mixing of the two resonance structures (Chart 1); this was tuned by an external electric field so as to provide a general description[12] of both external (solvent polarity) and internal (donor−acceptor strength) field effects, which had been pointed out by electric field-induced second harmonic (EFISH) generation measurements in solution.[13,14] With reference to the problem at issue, the theoretical studies of interest are those in which hyperpolarizabilities were evaluated according to the sum-over-states (SOS) approach based on perturbation theory.[15] Using the semiempirical INDO Hamiltonian, Marder et al.[10,12] carried out detailed SOS calculations of α, β and γ for a model merocyanine ($(CH_3)_2N-(CH{=}CH)_4-CHO$) as functions of a static electric field applied along the long molecular axis, determining the percentage contributions of the two resonance forms and thus the degree of π-bond order alternation (BOA). It was shown that the simple two-level model for the second-order polarizability, which amounts to assuming that the nonlinear polarization arises essentially from the lowest lying $^1(\pi\pi^*)$ CT state, accounts fairly well for a perturbation sum over thirty excited states.[10] This suggests that insofar as simple merocyanines are considered, the basic two-level model is sound from a theoretical point of view. Thus, in principle experimental determination of β based on the two-level model (eq 1) should be expected to provide reliable results, as well, for the molecules at issue. Values of μ_{ge} and E_{ge} can be obtained by standard spectroscopic methods, and $\Delta\mu_{eg}$, a rather problematic quantity, can be determined by various methods the most used of which is that based on measurements of solvatochromic shifts of absorption and fluorescence spectra.[7,8,16] The potentialities of the solvatochromic method for determining second-order polarizabilities were first probed on D−A systems such as p-nitroaniline and its analogs.[17,18]

Afterward, methods based on solvatochromism have been applied to many other organic NLO chromophores differing in the nature of the donor and/or acceptor groups as well as in the complexity of the connecting π-bridge usually containing aromatic groups.[19−27] However, at the best of our knowledge, experimental determinations of β by the solvatochromic method have never been reported for simple push−pull polyenes such as the streptomerocyanines (Chart 1).

In view of their importance as model D−A chromophores, a detailed test on the solvatochromic approach to the second-order polarizability of simple merocyanines seemed useful to us. So, we have undertaken a joined experimental and theoretical study on the first hyperpolarizability β, as well as linear polarizability α, of four merocyanines (Chart 2), in which both measurements and quantum-mechanical calculations have been carried out within the framework of the two-level model. In this respect, we note that (i) hyperpolarizabilities calculated by two-level or SOS approaches[10,12] are usually compared with EFISH measurements[13,14] and (ii) solvatochromic determination of β is hardly ever combined with quantum-mechanical calculations.[17−19,22−27]

CHART 2



At variance with refs 10−12 concerning mainly the dependence of linear and nonlinear polarizabilities on the degree of ground-state polarization (tuned by changing the environment) on a chromophore of fixed length, the present study aims at establishing the dependence of the "isolated-molecule" first- and second-order polarizabilities on the length of the conjugated bridge, the end donor/acceptor groups being the same. Moreover, we will provide a punctual molecule-by-molecule comparison between measured and calculated molecular (structural, electrical and optical) properties, in an attempt to go beyond a qualitative comparison between observed and calculated general trends.[28]

To gain this end, in this work we first of all carried out a detailed experimental investigation on the ground- and excited-state properties of the compounds in Chart 2. This encompasses measurement of ^{1}H NMR spectra, of electronic spectra in low-polarity solvents (providing approximate "isolated-molecule" values of μ_{ge} and E_{ge} for the transition from the ground state to the CT excited state), and the solvatochromic determination of the excited-state dipole moment μ_e according to Lippert's formulation of the Onsager model.[8,16] The ground-state dipole moments μ_g, required to obtain $\Delta\mu_{eg}$, were approximated using the experimental values reported in the literature for very similar merocyanines.[13] The solvatochromic approach to $\Delta\mu_{eg}$ was designed in such a way (narrow solvent-polarity interval taking n-hexane as the reference neutral medium) as to approximate the isolated-molecule values of $\Delta\mu_{eg}$. The resulting values of β_{CT} will be shown to be in very good agreement with those derived for similar compounds from EFISH measurements (in chloroform).[13]

Qualitatively good agreement was also found between the spectroscopically determined α_{CT}'s and literature data based on molar refraction measurements.[29]

All the measured properties were subjected to systematic theoretical analysis by quantum-mechanical calculations. In accordance with the end of the work, all calculations were performed in the isolated-molecule approximation. First, we analyzed the ground-state molecular structures by extensive full geometry optimizations at both semiempirical and ab initio level. The most reliable structures (as evidenced by the value of the bond length alternation (BLA) parameter) were obtained by calculations at the DFT (6-31G**/B3LYP) level. Using the so optimized geometries the linear optical properties (E_{ge}, μ_{ge}, $\Delta\mu_{eg}$), and hence the molecular polarizabilities α_{CT} and β_{CT} (eqs 1 and 2), were calculated by two semiempirical methods, ZINDO/S[30] and CS INDO,[31] differing in the choice of the electron repulsion integrals and the extension of the CI. It will be shown that the CS INDO method, when used with the Ohno−Klopmann[32] two electron integrals and CI including both singly- and doubly excited configurations, provides well bal-

TABLE 1: ^{1}H NMR Spectral Data for Merocyanines Mc3 and Mc4[a]

	solv	δ_1	δ_2	δ_3	δ_4	δ_5	δ_6	δ_7	δ_8	$\delta_{\text{N-Met}}$	$\delta_{\text{Met-CO}}$	J_{1-2}	J_{2-3}	J_{3-4}	J_{4-5}	J_{5-6}	J_{6-7}	J_{7-8}
Mc3	B	5.99	5.05	6.51	6.14	7.53	6.26			2.16	2.17	12.9	11.2	14.3	11.4	15.1		
	A	6.70	5.19	6.73	5.96	7.24	5.84			2.86	2.16	12.8	11.3	14.3	11.4	15.2		
Mc4	B	6.05	5.13	6.43	6.18	6.67	6.20	7.38	6.20	2.21	2.09	12.9	11.0	14.6	11.1	14.5	11.3	15.4
	A	6.61	5.16	6.52	5.97	6.73	6.12	7.24	5.96	2.82	2.17	12.8	11.2	14.5	11.3	14.5	11.4	15.3

[a] δ values are in ppm, J values in Hz. Solvents: B = benzene, A = acetonitrile.

anced optical properties thus reproducing quite well the experimentally derived values of α_{CT} and β_{CT}. The validity of the calculated α_{CT} and β_{CT} values will be shown to be also supported by comparison with SOS and finite field test calculations. An essential point of this work is that, insofar as simple merocyanines are considered, the solvatochromic method and quantum mechanical calculations can be driven to give consistent descriptions of the first hyperpolarizability β in the framework of the two level model.

2. Experimental Section

Merocyanines Mc1−4 were obtained from the Institute of Organic Chemistry of the Russian Academy of Sciences in Moscow and were used as received. All solvents were of spectroscopic grade and were dehydrated with molecular sieves when necessary. Static dielectric constants and refractive indexes of *n*-hexane/diethyl ether binary mixtures were calculated assuming an ideal mixing behavior from the properties of the pure solvents and their mole fractions. Absorption spectra were measured on a Varian Cary 100 UV−visible spectrophotometer. Fluorescence emission spectra were obtained with a Spex Jobin-Yvon Fluoromax2 spectrofluorometer and were corrected for the spectral sensitivity of the emission channel. Absorption and fluorescence measurements were performed on solutions having maximum optical densities at the main absorption band of 0.1−0.3, corresponding to concentrations of the order of 5×10^{-6} to 10^{-5} mol L^{-1}. At such concentrations no significant dye aggregation was spectroscopically observed.

All ^{1}H NMR spectra were measured on a Bruker Avance400 spectrometer equipped with a 5 mm broadband inverse probe head and operating at 9.4 T. The spectra were acquired by a standard pulse sequence. Proton−proton transient nuclear-Overhauser-effect (NOE) spectra were acquired using a two-dimensional standard NOESY sequence with a mixing time of 1.4 s. Proton−proton chemical-shift correlation spectra were obtained with a standard two-dimensional gradient-pulse COSY sequence.

3. Quantum-Mechanical Calculations

The ground-state properties of merocyanines Mc1−4 (fully optimized geometries, conformations and electrical dipole moments) were investigated by a variety of both semiempirical and ab initio procedures using the HyperChem as well as the Gaussian 03 computational packages.[33,34] The selected structures, derived from calculations at the DFT (B3LYP/6-31G** level, were used to calculate the excited-state electronic properties in the framework of two semiempirical INDO based schemes: Zerner's ZINDO/S CI[30] parametrized to reproduce UV−vis spectra (included in the HyperChem package) and our group's CS INDO CI[31] designed to deal with conformations (C) and spectra (S) of large conjugated molecules (homemade code). The CS INDO model, previously successfully used to describe ground and excited-state properties of a variety of systems (for a summary of the main applications see ref 6b), is applied here for the first time to the study of NLO properties.

The screening constants $k_{\mu\nu}$, peculiar to the CS INDO method,[6b,31,35] were chosen as follows: $k_{\sigma\sigma} = 1$, $k_{\pi\pi} = 0.5$, $k_{\sigma\pi} = 0.65$, $k_{n\pi} = 0.60$, $k_{n\sigma} = 0.72$, $k_{nn} = 0.68$. Unlike ZINDO/S, which adopts the Mataga−Nishimoto formula[36] for the two-electron repulsion integrals, the CS INDO calculations were carried out using the Ohno−Klopman parametrization.[32]

As concerns the CI procedure, the ZINDO/S method was applied in its standard version[33] including configuration interaction over singly excited configurations (SCI). For each molecule, we performed full SCI calculations.

A different CI scheme was used when the MOs were obtained by the CS INDO Hamiltonian. Here, we introduced the correlation effects by means of both single (S) and single + double (SD) excitations. Although a molecular-size dependent MO "active space" (from 12 + 6* MOs for Mc1 to 20 + 10* MOs for Mc4) was considered for building up the singly excited configurations, we adopted a smaller MO "active space" (3 + 3* MOs for all the molecules) for generating the doubly excited configurations.

The excited-state properties derived from these calculations procedures were used to evaluate first- and second-order polarizabilities of Mc1−4 according to the two-level model (eqs 1 and 2) and, only for trans Mc4 taken as an example, to the sum-over-states approach.

For comparison with two-level model results, linear polarizabilities of trans Mc1−4 were also calculated with the finite field method[1] (implemented in HyperChem) using the ground-state dipole moment obtained at the INDO (standard) SCF level with DFT-optimized geometries. Finite field calculation of higher order polarizabilities is not provided for in HyperChem. The Gaussian 03 package, on the other hand, includes finite field calculation of hyperpolarizabilities only at the ab initio level, thus giving values not directly comparable with those obtained by two-level or SOS approaches at the semiempirical level. The comparison between two-level model and finite field results has therefore been limited to the linear polarizabilities for internal consistency reasons.

4. Results and Discussion

4.1. Ground-State Structures and Dipole Moments. The first point to be cleared up concerns the stable conformations that Mc1−4 assume in solution. In ref 5a this question has already been answered for Mc1 and Mc2 by ^{1}H NMR spectroscopy. Here, we report the results of a similar ^{1}H NMR study carried out for merocyanines Mc3 and Mc4. The ^{1}H chemical shifts, δ, and H−H scalar spin coupling constants, J, of the merocyanines Mc3 and Mc4 in benzene and acetonitrile are given in Table 1 (see Figure 1 for the atom numbering). The reported assignment of the signals resulted unambiguously from COSY and NOESY spectra in both solvents. The values observed for Mc3 and Mc4 are in keeping with those given in ref 5a for Mc1 and Mc2 as well as those reported in the literature for merocyanines having a simple −CHO group as the acceptor.[37,38] The δ and J values relative to the protons of the central π bridge are of special interest as they are indicative of

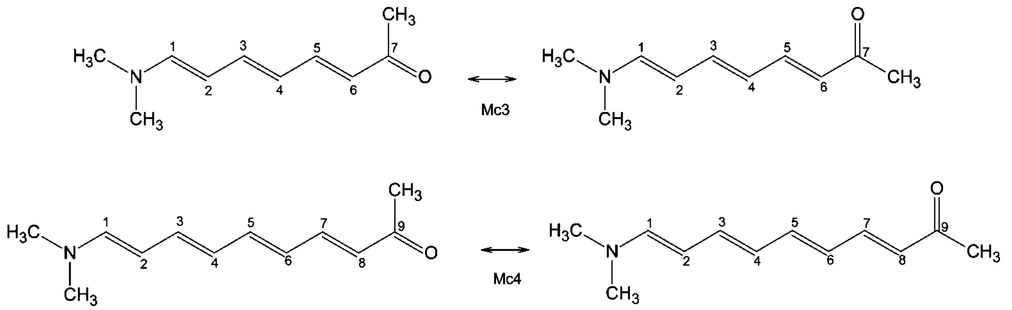


Figure 1. Structure and numbering of the carbon atoms in the conjugated bridge for trans and cis Mc3 and Mc4 (Chart 2).

TABLE 2: Bond Lengths of the Conjugated Chain of Merocyanine Mc2 Obtained by Full Geometry Optimizations Using Seven Semiempirical and Four ab Initio Methods (Atom Numbering in Figure 1)[a]

	N−1	1−2	2−3	3−4	4−5	5−O	BLA	μ_0/D
CNDO	1.384	1.344	1.430	1.342	1.441	1.278	0.0870	5.9326
INDO	1.387	1.346	1.432	1.345	1.443	1.283	0.0865	5.8654
MINDO/3	1.379	1.357	1.456	1.351	1.487	1.212	0.1020	6.1405
ZINDO/1	1.386	1.355	1.438	1.353	1.447	1.285	0.0840	7.2710
MNDO	1.402	1.364	1.460	1.355	1.494	1.231	0.1005	5.5322
AM1	1.376	1.362	1.438	1.345	1.466	1.240	0.0845	6.5867
PM3	1.425	1.348	1.447	1.341	1.482	1.220	0.1025	4.8570
STO-3G	1.403	1.328	1.474	1.323	1.510	1.225	0.1485	4.5071
6-31G**	1.357	1.342	1.450	1.334	1.476	1.199	0.1120	7.4277
DFT (STO-3G/B3LYP)	1.408	1.369	1.462	1.363	1.510	1.264	0.0960	5.9791
DFT (6-31G**/B3LYP)	1.361	1.365	1.434	1.356	1.466	1.228	0.0735	8.0670

[a] The last two columns report the bond length alternation parameter and the ground-state dipole moment, respectively.

the merocyanine-type electronic structure, having intermediate character between polyenes and symmetric cyanines.[5b] A detailed discussion can be found in ref 5a. Here, we simply stress the oscillatory behavior of the H−H coupling constants traceable to alternation of the C−C bond orders (BOA) and hence of the C−C bond lengths (BLA). As is well-known, the degree of oscillation is larger in polyenes[38] (where BLA is maximum), whereas it vanishes in symmetric cyanines[38,39] (characterized by equalized C−C bond lengths).

The molecular conformations were established by NOE measurements. Briefly, NOE was observed between H_1 and H_3, H_3 and H_5, H_5 and H_7, H_2 and H_4, H_4 and H_6, H_6 and H_8. Furthermore, NOE was observed between H_1 and H_2 on one side and the $N(CH_3)_2$ protons on the other and, with comparable intensities, between the CH_3CO protons and both H_5 and H_6 of Mc3 and H_7 and H_8 of Mc4. These results are fully consistent with those previously found for Mc1 and Mc2[5a] and indicate (Figure 1) that (i) the conjugated bridges connecting $N(CH_3)_2$ and CH_3CO groups have all trans configurations and (ii) at room temperature, the trans and cis conformations in Figure 1 are both present in comparable amounts in solutions of these compounds. Also, the appearance of single narrow signals for the CH_3CO and $N(CH_3)_2$ protons in both solvents, indicates that twisting about the C_6-C_7 bond of Mc3 and the C_8-C_9 bond of Mc4 and about the $N-C_1$ bonds of both dyes occurs rapidly compared with the NMR time scale.[40]

The ground-state properties were analyzed by extensive quantum mechanical calculations. We first tested the performances of a large selection of semiempirical and ab initio methods as far as geometry and BLA parameter are concerned. The test was performed by taking the trans isomer of Mc2 as a sample, and the values of the BLA, i.e., the difference between the average length of the "single" bonds and that of the "double" bonds in the central polyene-like fragment,[41,42] are given in Table 2 together with the ground-state dipole moments. The results of Table 2 can be commented by considering that the gas-phase structure of the reference polyene, butadiene, is characterized by alternating short (~1.34 Å) and long (~1.46 Å) bonds[43] and hence BLA = 0.12 Å. First of all, from Table 2 it is evident that the calculated values of BLA and μ_g are rather dispersed. This shows that the various methods provide rather different descriptions as far as the balance of the neutral and charge-separated forms is concerned (Chart 1). With the exception of the ab initio STO-3G calculation, giving a BLA exceeding the ceiling value of 0.12 Å, all the other methods predict BLA's below the experimental one of butadiene, even if the calculated values reflect a (lesser or greater) predominance of the neutral form, the average BLA being 0.093 Å. This value compares unfavorably with that determined by X-ray crystallography for streptomerocyanines with $n = 2$ or 3 (BLA = 0.05 Å).[44] It has been suggested that the structures found in the solid state are similar to those taken by merocyanines in polar solvents that are known to cause reduction in bond length alternation.[44] However, in the light of the moderate solvent polarity effects on the H−H spin coupling constants (Table 1 and ref 5a), the discrepancies between calculated (gas phase) and crystallographic structures of the polyene fragment appear to be on an average too high. Among the semiempirical methods, reasonable BLA's are obtained by CNDO, INDO, ZINDO/1 and AM1 Hamiltonians (0.08−0.09 Å). At the ab initio level, the BLA's appear to be sensitive to the size of the AO basis set and to correlation effects. As a matter of fact, the "best" BLA (0.073Å) was obtained by the calculation at the DFT (6-31G**/B3LYP) level.

On the basis of this analysis, we decided to calculate DFT(6-31G**/B3LYP)-optimized geometries of trans and cis Mc1−4 merocyanines to be used in the ZINDO/S and CS INDO CI calculations of the molecular polarizabilities according to the two-level model (section 4.2). Such geometries are reported in detail in Table S1 (Supporting Information). As an example, the optimized geometries of trans and cis Mc3 are represented in Figure 2. The geometries of the other merocyanines are

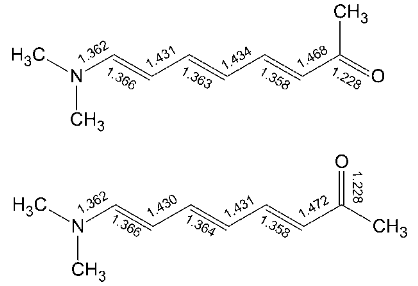


Figure 2. Geometries of trans and cis Mc3 obtained by full optimization at the DFT (6-31G**/B3LYP) level.

TABLE 3: Measured Linear Optical Properties and First-Order Polarizabilities (α_{XX}) of Merocyanines Mc1−4

	ν_{ge}[a] (cm^{-1})	f[b]	μ_{ge}[c] (D)	α_{XX}[d] (10^{-24} cm^3)
Mc1	35000	0.38	4.80	6.63
Mc2	29960	0.50	5.96	11.94
Mc3	26640	0.67	7.34	20.50
Mc4	24400	0.87	8.71	31.31

[a] Wavenumbers of the absorption maxima in *n*-hexane. [b] Oscillator strengths in ether, $f = 4.32 \times 10^{-7} \int \varepsilon(\nu)\, d\nu$. [c] $\mu_{ge} = (f/4.7016 \times 10^{-7} \nu_{ge})^{1/2}$. [d] From eq 3 expressing μ_{ge} in esu·cm and E_{ge} in ergs.

essentially copies of those given in Figure 2. The general conclusion is that (i) in both conformational isomers revealed by H NMR spectroscopy, the three molecular fragments (D, A and polyene) are coplanar and (ii) the polyene fragment is characterized by all trans configuration with alternating shorter (~1.36 Å) and longer (~1.43 Å) bonds and hence BLA ≅ 0.07 Å (to be compared with a BLA = 0.11 Å determined by X-ray crystallography for octatetraene[45]). In Mc1 the polyene fragment is reduced to an ethylene bridge with $R_{C=C} \cong 1.36$ Å.

The same calculations predict the cis arrangement of the acceptor group, $-CH_3CO$, to be more stable with a $\Delta E_{cis-trans}$ going from −9.6 kJ mol^{-1} for Mc1 to −4.4 kJ mol^{-1} for Mc4. So, although NMR data are consistent with an almost unitary [cis]/[trans] equilibrium ratio in solution, calculations suggest that in the gas phase the cis form should be predominant (at ordinary *T*).

At last, we have to take into consideration the ground-state dipole moments, the knowledge of which is a basic requirement in any study of the second-order polarizabilities. In this work we could not perform dipole moment measurements. Simply, we deduced the Mc1−4 dipole moments from those reported by Marder et al.[13] for three unsubstituted merocyanines $R_2N-(CH{=}CH)_n-CHO$ with $n = 1, 2, 3$, combining experimental (NMR) evidence and theoretical considerations. First of all, our NMR study has shown that replacing the formyl ($-CHO$) with the acetyl ($-CCH_3O$) acceptor leaves the electronic structure of the merocyanines essentially unchanged.[37,38] So, we can confidently attribute to the trans components of Mc1−3 the μ_g values given in ref 13 for the three unsubstituted merocyanines having no doubt trans conformation (6.30, 6.50 and 6.90 D). By simple linear extrapolation the dipole moment of trans Mc4 was assumed to be equal to 7.30 D. Reasonable μ_g values for the cis components were then obtained by considering that all the tested quantum mechanical methods, although they may give rather different individual μ_g's (Table 2), predict very similar $\mu_g^{cis}/\mu_g^{trans}$ ratios with a mean value near 0.80 (Supporting Information, Table S2). Accordingly, we assigned the cis forms of Mc1 to Mc4 the following μ_g values: 5.04, 5.20, 5.52 and 5.84 D. Finally, because NMR data indicate that cis and trans forms are present in comparable abundances, from the formula $\mu_g^2 = \{\mu_g^{trans2} + \mu_g^{cis2}\} \times 0.5$, it is straightforward to deduce that in fluid solution the observed μ_g's should be about 5.56 D (Mc1), 5.89 D (Mc2), 6.25 D (Mc3) and 6.61 D (Mc4). It is to be pointed out that the adopted dipole-moment set is characterized by a modest increase of μ_g with increasing conjugation length, in keeping with the experimental results obtained on other series of push−pull polyenes.[46] On the other hand, the μ_g values of both trans and cis Mc1−4 obtained by DFT calculations exhibit a rather fast increase with the length of the conjugated system (see Table S2 of the Supporting Information). This may be viewed as an indication that the DFT (6-31G**/B3LYP) scheme overestimates to a certain degree the electron transfer from donor to acceptor in the ground state. The same phenomenon occurs, yet in smaller measure, when dipole moments are calculated at the ZINDO/S and CS INDO level using the DFT geometries (Supporting Information, Table S2). Relatively speaking, the best agreement with experiment was obtained by calculations at the CS INDO SCF level.

4.2. Molecular Polarizabilities. In this section we report the experimentally derived values of the linear polarizability α_{CT} and first hyperpolarizabilility β_{CT} of the Mc1−4 merocyanines as obtained in the framework of the two-level model using UV−vis absorption/emission spectroscopy and the solvatochromic method for the determination of the dipole moment of the lowest lying $^1(\pi\pi^*)$ CT excited state. We then report the α_{CT} and β_{CT} values derived from the computational version of the two-level model using the ZINDO/S and the CS INDO CI methods and analyze them in comparison with the experimental values. Considering that in Mc1−4 the charge-transfer direction is essentially coincident with the molecular long axis (here taken as X-axis), α_{CT} and β_{CT} can be indicated as α_{XX} and β_{XXX} whose explicit expressions are

$$\alpha_{XX} = 2\frac{\mu_{ge}^{2}}{E_{ge}} \qquad (3)$$

and

$$\beta_{XXX} = 6\frac{\mu_{ge}^{2}}{E_{ge}^{2}}\Delta\mu_{eg} \qquad (4)$$

Equations 3 and 4 are formally the single term expressions to which the SOS expansions of α_{XX} and β_{XXX} simplify when only the ground state and the lowest lying CT excited state are considered.[10]

4.2.1. CT-Transition Properties and Linear Polarizability α. The two-level model description of linear polarizabilities involves only energy (E_{ge}) and dipole moment (μ_{ge}) of the CT $\pi \rightarrow \pi^*$ transition responsible for the first intense absorption band. However, in merocyanines, due to the presence of a $>C{=}O$ group, a $^1(n\pi^*)$ state may lie below the CT $^1(\pi\pi^*)$ state. As a matter of fact, the weak fluorescence emission of the studied merocyanines (see later) as well as ZINDO/S and CS INDO CI calculations indicated unambiguously a $^1(n\pi^*)$ state to be the first singlet excited state. The energy difference between CT $^1(\pi\pi^*)$ and $^1(n\pi^*)$ states decreases with increasing length of the conjugated system and almost vanishes in Mc4. However, the presence of forbidden $^1(n\pi^*)$ states does not affect either the quantities involved in linear polarizability or the solvent shift of the absorption maxima. So, from now on our attention will be focused on the CT $\pi \rightarrow \pi^*$ transition. In short, the pertinent spectroscopic parameters measured in an apolar solvent are collected in Table 3 together with the first-order

TABLE 4: Linear Optical Properties and First-Order Polarizabilities of Mc1-4 (Trans Forms) Calculated by ZINDO/S (a), CS INDO SCI (b), CS INDO SDCI (c) and Finite Field with INDO Standard Hamiltonian (d) Methods

	method	$\tilde{\nu}_{ge}$ (cm^{-1})	μ_{ge} (D)	α_{XX} (10^{-24} cm^3)
Mc1	a	36192	6.224	10.78
	b	39663	6.262	9.96
	c	38392	5.238	7.20
	d			9.21
Mc2	a	30642	8.678	24.75
	b	34447	8.684	22.04
	c	33344	6.782	13.89
	d			17.76
Mc3	a	27185	10.812	43.30
	b	30820	10.750	37.76
	c	30173	8.508	24.16
	d			29.31
Mc4	a	24809	12.718	65.65
	b	28198	12.530	56.07
	c	27793	10.048	36.58
	d			43.61

polarizabilities obtained from eq 3. The so obtained values of α_{XX} can be considered as two-level model approximations to the "gas-phase" polarizabilities of Mc1−4. The rise of α_{XX} with n (i.e., with the length of the polyene fragment) is generically parabolic. With the caution required by the use of only four data points, we can say that the rise in linear polarizability follows the relationship $\alpha_{XX} \propto n^{1.3}$. Validation of the α_{XX}'s in Table 3 would require the knowledge of linear polarizabilities of Mc1−4 measured independently, i.e., out of the two-level model approximation. We do not have such values, but we can refer to the average polarizabilities of two streptomerocyanines with $n = 1, 2$ derived from molar refraction measurements in medium-high polarity solvents.[29] By extrapolation of the data of ref 29 to a low-polarity medium ($\varepsilon \approx 3$, ε = solvent static dielectric constant) we estimated α to be $(10 \pm 4) \times 10^{-24}$ cm^3 for $n = 1$ and $(14 \pm 4) \times 10^{-24}$ cm^3 for $n = 2$. Within the large margin of error, these estimates are consistent with the experimental two-level model values obtained for Mc1 and Mc2 (Table 3).

With regard to the two-level model α_{XX}'s, the performance of a quantum mechanical method depends on its ability to provide at the same time good predictions of E_{ge} and μ_{ge}, which is not so easy for most current methods. The three tested approaches (ZINDO/S, CS INDO SCI and CS INDO SDCI) give quite different results in virtue of the different parametrizations and CI extensions. Detailed numerical results obtained for the trans forms of Mc1−4 are reported in Table 4. The results concerning the cis forms, featuring essentially the same trends, can be found in Supporting Information, Table S3. Here we will briefly comment on the results by the aid of Figures 3−5 where $\tilde{\nu}_{ge}$, μ_{ge}, and α_{XX} values calculated for the trans forms are compared with experimental values. ZINDO/S, using Mataga−Nishimoto electron repulsion integrals and CI limited to singly excited configurations, reproduces very well the transitions energies (Figure 3) but it largely overestimates transition dipole moments (Figure 4), thus leading to poor predictions for α_{XX}. To go beyond the ZINDO/S results, one should gain more flexibility by changing from Mataga−Nishimoto to Ohno−Klopman two-center two-electron integrals γ_{AB} and performing CI's of different sizes. This was carried out using the CS INDO method in conjunction with S and S+D CI's. Not surprisingly, CS INDO SCI overestimates both transition energies and transition dipole moments (the latter failure being related essentially to the SCI). On the other hand, with CS INDO SDCI the overestimation of the transition energy is mitigated (Figure 3) and, at the same time, the transition dipole moments are greatly improved (Figure 4). Thus, CS INDO SDCI warrants a better balancing of the quantities involved in the calculation of the linear polarizabilities. This is emphasized in Figure 5 where the α_{XX} values of trans Mc1−4 obtained by the three theoretical two-level-model approaches are compared with those derived from the electronic spectra (Table 3). Figure 5 shows that the ZINDO/S calculation recipe, based on the Mataga−Nishimoto γ_{AB}'s and CI limited to single excitations, is not very adequate as far as the prediction of linear polarizabilities is concerned. On the contrary, the CS INDO method adopting Ohno−Klopman γ_{AB}'s reproduces fairly well the experimental

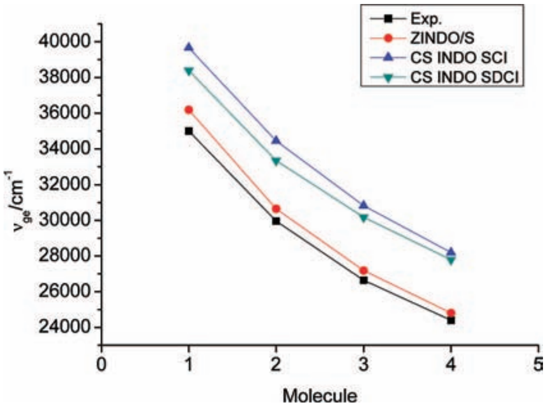


Figure 3. Comparison between the locations of the CT absorption bands of Mc1−4 in *n*-hexane and those calculated for the trans forms in the gas-phase approximation.

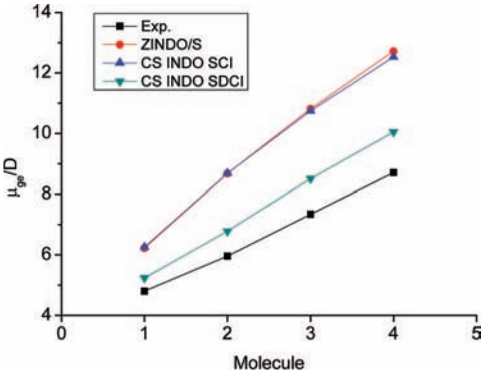


Figure 4. Comparison between the CT transition dipole moments of Mc1−4 in ether and those calculated for the trans forms in the gas-phase approximation.

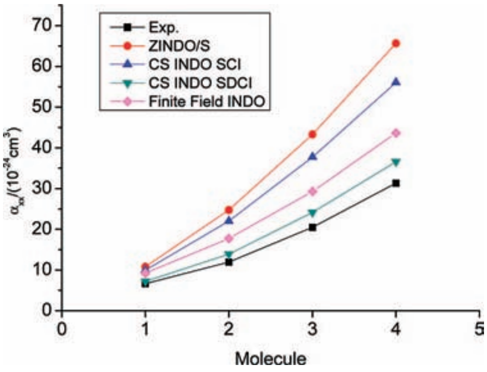


Figure 5. Linear polarizabilities of Mc1−4 experimentally derived and calculated (trans forms) within the framework of the two level model. Finite field values obtained at the standard-INDO level are also reported.

TABLE 5: Linear Polarizability (10^{-24} cm^3) of Trans Mc4 Calculated According to the Two-Level Model (TLM) and the Sum-Over-States (SOS) Method

	ZINDO/S	CSINDO SCI	CS INDO SDCI
α_{XX}^{a}(TLM)	65.7	56.1	36.6
α_{XX}^{b}(TLM)	63.5	53.9	36.0
α_{XX}^{c}(SOS)	66.2	55.4	47.3
α_{XX}^{d}(SOS)	66.3	55.8	47.8

[a] From eq 3 using the module of $\vec{\mu}_{ge}$ (see Table 4). [b] From eq 3 using the x component of $\vec{\mu}_{ge}$. [c] Sum over 10 excited states, $\alpha_{XX} = 2\sum_e (\mu_{ge}^X)^2/E_{ge}$. [d] Sum over 20 excited states, α_{XX} i.c.s.

two-level model α_{XX} values provided that double excitations are included in the CI calculations. One might object that in Figure 5 the calculated α_{XX} values correspond to the trans Mc1−4 forms and the experimental values are representative of mixtures, most likely 1:1, of trans and cis forms. On the other hand, as can be verified comparing Table 4 with Table S3 (Supporting Information), the E_{ge} and μ_{ge} values calculated at the CS INDO SDCI level for the cis and trans arrangements of the $-CH_3CO$ group are almost superimposable (some appreciable differences were found only at the ZINDO/S and CS INDO SCI levels). In other words, according to theory, the linear polarizabilities of Mc1−4 should be expected to be not very dependent on the composition of the conformational mixture. Finally, it should be noted that, in spite of quite different absolute values, a general rising law $\alpha_{XX} \propto n^{1.3}$ is followed also by the linear polarizabilities derived from the three theoretical approaches.

Interestingly, the α_{XX} values derived from the finite field calculations using the DFT-optimized geometries and the INDO standard Hamiltonian (see Table 4 and Figure 5) are in between the CS INDO SDCI and the CS INDO SCI two-level model values. In principle finite field results should be directly compared with those obtained by the CS INDO SCI calculations, because both approaches are based on a simple SCF description of the ground state (i.e., effects of electron correlation on the ground-state are ignored). In practice, the finite field α_{XX}'s are somewhat lower than the CS INDO SCI ones and increase a bit less rapidly with n, $\alpha_{XX} \propto n^{1.23}$. The differences can be at least partly attributed to the γ_{AB} integrals that are calculated theoretically in INDO and by the Ohno−Klopman formula in CS INDO. Not surprisingly, the ZINDO/S method, parametrized to optimize merely the transition energies, gives α_{XX}'s that show the largest divergence from the finite field values. At last, it is to be noted that the finite field linear polarizabilities are appreciably, yet not dramatically, higher than those determined within the two-level model using experimental values of μ_{ge} and E_{ge} (Table 3 and Figure 5). Considering the relative crudeness of the finite field treatment, such differences might be not very significant. On the contrary, they might give indirect evidence of significant contributions from higher excited states missed within the two-level model. The electronic spectra appear to leave out this possibility, because (i) only weak absorptions are observed in the near UV region and (ii) good matching is observed between absorption and excitation spectra for the fluorescent Mc4 (see later), a fact that leaves out the presence of significant transitions other than the lowest-energy $\pi \rightarrow \pi^*$ under the first absorption band. According to calculations, however, the point is less clear, as it comes out from Table 5 where the two level model results for Mc4 are compared with those obtained by SOS calculations over 10 and 20 states. First, we note that sums over 10 states are enough to obtain good convergence of the α_{XX} values with all of the three approaches. On the other hand, converged SOS and two-level model results are almost coincident when using SCI descriptions, whereas at the SDCI level the converged SOS value of α_{XX} is somewhat higher due to a not very large, yet significant, contribution from a "new" CT-type state located ~6000 cm^{-1} above the lowest lying $^1(\pi\pi^*)$ state. However, the SOS value (47.3×10^{-24} cm^3) obtained with the CS INDO SDCI description remains lower than those derived from SCI treatments and is comparable with that obtained at the finite field (INDO) level (43.6×10^{-24} cm^3) (Table 4).

4.2.2. Solvatochromism and First Hyperpolarizability β.

In this section we will be concerned with solvatochromic determination and theoretical evaluation of $\Delta\mu_{eg}$, the difference between the CT excited-state and the ground-state dipole moment, involved in the two-level model expression of the first hyperpolarizability together with $1/E_{ge}^2$ and μ_{ge}^2(eq 4). In subsection 4.2.2.1, the determination of μ_e (and hence $\Delta\mu_{eg}$) is based on the solvent shift of the absorption maximum and the analysis is extended over the whole set of merocyanines Mc1−4. To check the consistency of the solvatochromic approach, in subsection 4.2.2.2 we report μ_e ($\Delta\mu_{eg}$) values determined using solvent spectral shifts of both absorption and fluorescence. In this case, however, the study is limited to Mc4 because the shorter homologues are characterized by too weak fluorescence emission.

4.2.2.1. Approach Based on the Absorption Spectra. To extract the excited-state dipole moment from the observed solvent induced spectral shifts, we adopted the classic Lippert theory[47] according to which the solvent dependent location of the absorption bands is expressed as

$$\tilde{\nu}_A = -\frac{2\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)}{hca^3}[f(\varepsilon) - f(n^2)] - \frac{2(\mu_e^{\ 2} - \mu_g^{\ 2})}{hca^3}f(n^2) \quad (5)$$

with

$$f(\varepsilon) = \frac{\varepsilon - 1}{2\varepsilon + 1} \qquad \text{and} \qquad f(n^2) = \frac{n^2 - 1}{2n^2 + 1}$$

where ε is the static dielectric constant and n the refractive index of the solvent. Lippert's theory, as well as other more or less sophisticated approaches,[8,16] derives from a perturbation theory treatment where solvent−solute interactions are described in terms of the simple reaction-field method (Onsager model). Equation 5 represents a simplified formulation that accounts for the effects due to change of the solute dipole moment (first term) and instantaneous solvent polarization (second term) induced by vertical g → e excitation. Excitation-induced changes in solute polarizability, solvent-dipole reorientation and dispersion interactions are neglected. To sum up, excited-state dipole moments determined using eq 5 should be regarded as approximations to the dipole moment of the Franck−Condon CT excited states. However, direct use of eq 5 is inconvenient because the two terms have different dependence, linear and quadratic, on the excited-state dipole moment. To avoid this difficulty, following ref 8 we approximated $\mu_e^{\ 2} - \mu_g^{\ 2} = (\mu_e + \mu_g)(\mu_e - \mu_g)$ by $2\mu_g(\mu_e - \mu_g)$, thus obtaining the easy-handled equation

$$\tilde{\nu}_A = -\frac{2\vec{\mu}_g(\vec{\mu}_e - \vec{\mu}_g)}{hca^3}[f(\varepsilon) + f(n^2)] = -m_A[f(\varepsilon) + f(n^2)] \quad (6)$$

In practice, the value of $\tilde{\nu}_A$ was measured for each merocyanine in a proper set of solvents, and the data were fitted to eq 6 by a linear regression thus obtaining the m_A constant. Thereby the excited-state dipole moment comes out to be expressed as

$$\mu_e = m_A \frac{hca^3}{2\mu_g \cos\phi} + \frac{\mu_g}{\cos\phi} \tag{7}$$

where a is the radius of the cavity surrounding the solute molecule point dipole and φ is the angle formed by $\vec{\mu}_e$ and $\vec{\mu}_g$. To estimate the cavity radius a, the molecular volume was calculated, for each molecule, adopting the grid method[48] (implemented in Hyperchem[33]) based on the use of the van der Waals radii of the atoms. The value so obtained was then used as the volume of the "equivalent" sphere of radius a. The cavity radii provided by this approach were 3.07, 3.30, 3.50 and 3.67 Å for Mc1 to Mc4 merocyanines. Onsager radii, however, should be considered as parameters to be validated comparing the results (here first hyperpolarizabilities) with experimental data from other sources (e.g., EFISH data) and/or with those obtained by more sophisticated solvatochromic approaches avoiding explicit introduction of the cavity radius (see later). As to the angle φ, calculations indicate that $\vec{\mu}_e$ and $\vec{\mu}_g$ are not parallel but, as expected for our quasi-linear molecules, angulation is rather small especially for Mc3 and Mc4. We adopted a single average value, $\varphi = 13°$.

The solvatochromic determination of μ_e (requiring μ_g to have been determined independently) was performed adopting two different solvent choices: (i) a solvent set spanning a wide range of polarity and (ii) binary *n*-hexane/diethyl ether mixtures. The solvents employed for the first procedure were chosen for their low hydrogen bond donor abilities and rejecting aromatic and polychlorinated aliphatic solvents, which may give rise to anomalous shifts due to their high electronic polarizabilities.[49] The lowest-energy bands of the four streptomerocyanines were usually structureless and symmetric (in a wavelength representation): the conservation of their shape throughout the solvent choice was such as to regard band maxima reliable solvatochromic source data for μ_e determination. The solvent dependence of absorption band maxima of Mc1−4 is summarized in Supporting Information, Figure S1. Here, we first note that, as expected, merocyanines Mc1−4 exhibit a marked positive solvatochromism. However, the negative slopes of $\tilde{\nu}_A$ vs $[f(\varepsilon) + f(n^2)]$ obtained by the whole solvent choice show a nonmonotonic behavior with the chromophore length: they strongly increase moving from Mc1 (-2320 cm^{-1}) to Mc2 (-7268 cm^{-1}) and then slightly decrease for Mc3 (-7095 cm^{-1}) and, more, for Mc4 (-6100 cm^{-1}). On the other hand, in *n*-hexane/diethyl ether mixtures (Supporting Information, Figure S2) all (negative) slopes are quite markedly lower and exhibit a "saturating" behavior: -1598, -4186, -4819 and -4713 cm^{-1} for the four dyes. Also, smoother data point distributions are obtained in these binary mixtures, compared with the rather scattered ones found with the whole solvent choice; a comparison is shown for Mc4 in Figure 6. All plots exhibit slight downward curvatures. This implies that, for a given solute, solvatochromic slopes and μ_e are larger in more polar media, where the weights of the charge-separated limit structures of the dyes are larger. Slopes "at the origin" of these plots were obtained by including the four lowest-polarity mixtures (including *n*-hexane) in linear least-squares fittings, with the purpose of producing values of μ_e attributable to the dyes in an apolar solvent, and amenable to comparison with those calculated for isolated molecules. As a matter of fact, with this procedure the solute is subjected to weak solvent reaction fields (compared to the unperturbed system) in keeping with perturbation theory requirements. Such a condition is hardly satisfied by solvatochromic slopes obtained with the whole solvent choice. On the contrary, by comparing spectroscopically derived and calculated results, we will soon demonstrate that, once a few requisites are fulfilled, the assumption that hyperpolarizabilities deduced from low-polarity limit solvatochromic slopes are representative of the isolated-molecule limit values is sound and reliable.

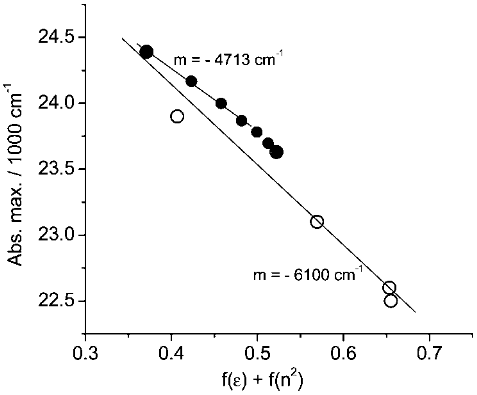


Figure 6. Maximum absorption wavenumbers of Mc4 in (below, from left to right) *n*-hexane, cyclohexane, diethyl ether, butyronitrile and acetonytrile, and (above) in *n*-hexane/diethyl ether mixtures with hexane volume fractions (from left to right): 1, 0,83, 0.67, 0.5, 0.33, 0.17, 0.

The values of m_A obtained by the two procedures for Mc1−4 are reported in Table 6 together with the resulting values of μ_e (eq 7), $\Delta\mu_{eg}$ (using the estimated μ_g's given in the first column) and first hyperpolarizabilities β_{XXX}. Table 6 shows that the $\Delta\mu_{eg}$ values obtained for Mc1−4 by the two solvatochromic procedures reflect magnitude and behavior of the corresponding solvatochromic slopes.

In particular $\Delta\mu_{eg}$'s derived from procedure 1 (whole solvent choice) are markedly higher than those obtained by procedure 2 and show nonmonotonic behavior. The resulting values of β_{XXX}, obtained by eq 4 using spectroscopic data of Table 3, have also markedly higher values increasing rapidly and quasi linearly with n (1−4). Both values and n-dependence fit poorly the EFISH data in CHCl$_3$ reported in the literature for three unsubstituted merocyanines with $n = 1, 2, 3$.[13] This can be taken as indication that the excited-state dipole moment deduced from solvatochromic procedures over wide ranges of solvent polarity likely corresponds to a sort of average value, due to the marked changes in the electronic structure of the solute induced by marked changes in the solvent dielectric constant.[50] Interestingly, β_{XXX} values provided by procedure 2 fit very well the EFISH values[13]as far as merocyanines with $n = 1, 2, 3$ are concerned.[51] The β_{XXX}'s appear to rise with n more rapidly than the α_{XX}'s (Table 3). This behavior is implicit in the two-level model relationship $\beta_{XXX} = \alpha_{XX}\Delta\mu_{eg}/E_{ge}$, where both $\Delta\mu_{eg}$ and $1/E_{ge}$ rise with n. Approximately, the rise in β_{XXX} follows the relationship $\beta_{XXX} \propto n^{2.1}$, in qualitively good agreement with the n-dependence of EFISH β_{XXX}'s reported for similar push−pull polyenes.[52] On the whole, these results suggest that the solvatochromic slopes obtained using a few lowest-polarity *n*-hexane/diethyl ether mixtures may actually provide the excited-state dipole moment of the solute in the reference apolar solvent (here *n*-hexane). The good agreement with the EFISH data in CHCl$_3$ gives support to the validity of the two-level model as well as to the consistency of the approximations (and parametrizations) adopted in our solvatochromic approach, at least as far as the D−A polyenes under study are concerned. Further validation of the results of Table 6 will be attempted in next section in terms of solvent shifts of both absorption and fluorescence bands of Mc4.

As it has been done in section 4.2.1 for the linear polarizabilities, we now go on to compare the first hyperpolarizabilities

TABLE 6: First Hyperpolarizabilities (β_{XXX}) of Merocyanines Mc1−4 from Spectroscopic Data (μ_{ge} and E_{ge}, Table 3) and Solvatochromic Determination of the Differences between CT Excited- and Ground-State Dipole Moments ($\Delta\mu_{eg}$)[a]

	μ_g[b] (D)	method[a]	m_A[c] (cm^{-1})	μ_e (D)	$\Delta\mu_{eg}$ (D)	β_{XXX}[d] (10^{-30} cm^5 esu^{-1})	$\beta(0)$[e] (10^{-30} cm^5 esu^{-1})
Mc1	5.56	1	2320	6.99	1.43	4.08	2.9
		2	1598	6.59	1.03	2.94	
Mc2	5.89	1	7268	10.57	4.68	28.15	16.5
		2	4186	8.66	2.77	16.66	
Mc3	6.25	1	7095	11.38	5.13	60.82	41.0
		2	4819	9.79	3.54	41.42	
Mc4	6.61	1	6100	11.44	4.83	93.56	
		2	4713	10.38	3.77	73.03	

[a] Solvatochromic slopes were determined using (1) the whole solvent set and (2) the four less polar *n*-hexane/diethylether mixtures. [b] Estimated values of the ground-state dipole moments for 1:1 trans−cis mixtures in low polarity solvent. [c] Solvatochromic slopes obtained by fitting absorption wavenumbers ν_a to eq 6 by means of linear regressions. [d] From eq 4 and data of Table 3 expressing μ_{ge} and $\Delta\mu_{eg}$ in esu·cm and E_{ge} in ergs. [e] From ref 13 EFISH data in CHCl$_3$ solution for streptomerocyanines with $n = 1, 2, 3$.

TABLE 7: Excited-State Dipole Moments (μ_e), Differences between CT Excited- and Ground-State Dipole Moments ($\Delta\mu_{eg}$) and First Hyperpolarizabilities (β_{XXX}) Calculated for the Trans Conformations of Mc1−4 by ZINDO/S (a), CS INDO SCI (b) and CS INDO SDCI (c) Methods

	method	μ_e (D)	$\Delta\mu_{eg}$ (D)	β_{XXX} (10^{-30} cm^{5}esu^{-1})
Mc1	a	11.289	4.112	18.50
	b	11.476	4.189	15.88
	c	10.857	3.638	10.30
Mc2	a	13.972	5.544	67.63
	b	13.503	5.005	48.38
	c	12.830	4.222	30.04
Mc3	a	16.028	6.674	160.56
	b	14.894	5.490	101.58
	c	14.737	5.073	61.35
Mc4	a	17.501	7.423	296.69
	b	15.746	5.652	169.74
	c	16.549	6.094	121.14

determined by the solvatochromic method with those calculated by application of the two-level scheme at the ZINDO/S, CS INDO SCI and CS INDO SDCI levels. Detailed values of μ_e, $\Delta\mu_{eg}$ and β_{XXX} calculated for the trans forms (from eq 4 using μ_{ge} and $\tilde{\nu}_{ge}$ values given in Tables 4) by the three methods are reported in Table 7. The same details concerning the cis forms are given as Supporting Information (Table S4).

For the sake of brevity the results can be discussed by reference to Figures 7 and 8 where the values of $\Delta\mu_{eg}$ and β_{XXX} calculated for the trans forms of Mc1−4 are plotted together with the experimentally derived ones determined by the more reliable solvatochromic approach (procedure 2).

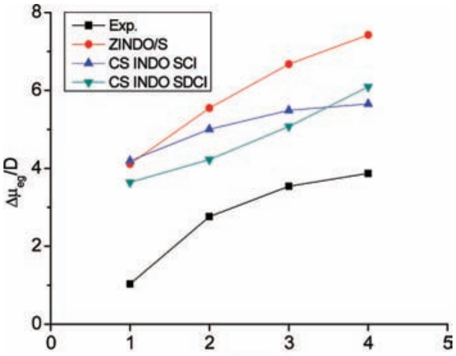


Figure 7. Differences between excited- and ground-state dipole moments of Mc1−4 obtained by the solvatochromic method and those calculated for the trans forms in the gas-phase approximation.

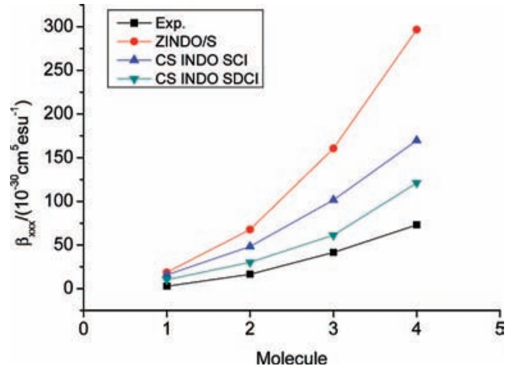


Figure 8. First hyperpolarizabilties of Mc1−4 experimentally derived and calculated (trans forms) within the framework of the two-level model.

Figure 7 shows that all calculations give $\Delta\mu_{eg}$'s higher than those deduced from solvatochromic measurements. CS INDO SDCI provides a little lower values for Mc1−3, but it does not reproduce the saturating behavior of the solvatochromic $\Delta\mu_{eg}$'s, which is better described at the CS INDO SCI level. The effect of including doubly excited configurations was found to be rather weak in the case of the cis forms (Supporting Information, Table S4) where $\Delta\mu_{eg}$'s derived from SCI and SDCI calculations show much more similar behaviors. However, the different CI effects on the values of $\Delta\mu_{eg}$ have relatively little importance in reference to the prediction of first hyperpolarizabilities. As a matter of fact, the most important characteristic shared by experimental and theoretical $\Delta\mu_{eg}$'s is that they increase rather slowly with the lengthening of the conjugate system compared with the sharp increase of the $\mu_{ge}{}^2$ and $1/E_{ge}{}^2$ factors entering the two-level model expression of β_{XXX}. A general comparison between calculated and experimental two-level model hyperpolarizabilities β_{XXX} of Mc1−4 is exemplified by Figure 8, where the β_{XXX} values calculated for the trans forms are plotted together with the ones obtained for the equilibrium trans−cis mixtures by the spectroscopic procedure (2). An almost equal general picture, omitted here for brevity, was obtained using the calculated values of the cis forms (Supporting Information, Table S4). From Figure 8 we can conclude that β_{XXX} values of Mc1−4 determined by a solvatochromic approach designed to give the molecular first hyperpolarizabilities in an apolar solvent can be satisfactorily reproduced by semiempirical two level model calculations in the free molecule approximation. The best recipe in this respect is that combining use of Ohno−Klopman repulsion integrals and CI including both singly- and doubly-excited configurations. As we have noted in section 4.2.1, the improvements obtained by inclusion of diexcited configurations concern mainly the prediction of the transition dipole moments.

TABLE 8: First Hyperpolarizability (10^{-30} cm^5 esu^{-1}) of Trans Mc4 Calculated According to the Two-Level Model (TLM) and the Sum-Over-States (SOS) Method

	ZINDO/S	CSINDO SCI	CS INDO SDCI
$\beta_{xxx}{}^a$(TLM)	296.7	169.7	121.1
$\beta_{xxx}{}^b$(TLM)	301.6	174.6	128.4
$\beta_{xxx}{}^c$(SOS)	305.1	176.2	142.6
$\beta_{xxx}{}^d$(SOS)	304.5	176.3	143.3

[a] From eq. 4 using the module of $\vec{\mu}_{ge}$ and $\Delta\vec{\mu}_{eg}$ (see Table 7). [b] From eq. 4 using the *x* component of $\vec{\mu}_{ge}$ and $\Delta\vec{\mu}_{eg}$. [c] Sum over 10 excited states, $\beta_{XXX} = 6\sum_e (\mu^X_{\rm ge})^2\Delta\mu^X_{\rm eg}/E_{\rm ge}{}^2$. [d] Sum over 20 excited states, β_{XXX} i.c.s.

At last, we note that, independently of their absolute values, the β_{XXX}'s derived from the three theoretical approaches rise proportionally to about n^2 in keeping with the experimental ones.

As has been done for the α_{XX}'s, we now compare (Table 8) the β_{XXX} two-level model values with those derived from SOS calculations over 10 and 20 excited states, taking Mc4 as an example. Sums over 10 states appear to be enough to attain satisfactory convergence with the three approaches. In this case, too, converged SOS and two-level model results obtained by SCI descriptions are almost equal, whereas at the SDCI level the SOS value is somewhat higher than the two-level one due to the occurrence of the already mentioned higher-energy ($\tilde{\nu} \cong$ 34000 cm^{-1}) state characterized by appreciable values of transition dipole moment ($\mu^X_{\rm ge} = 5.6$ D) and difference between excited- and ground-state dipole moment ($\Delta\mu^X_{\rm eg} = 2.6$ D). The SOS SDCI value, however, is sensibly lower than those predicted at the SCI level.

4.2.2.2. Approach Based on the Absorption and Fluorescence Spectra. In the previous section, the values of $\Delta\mu_{\rm eg}$ derived from the shifts of the absorption maxima over four lowest-polarity *n*-hexane/diethyl ether mixtures were shown to give first hyperpolarizabilities in very good agreement with EFISH data in CHCl$_3$ reported in the literature for systems very similar to Mc1−4. Although such a result is quite encouraging, any attempt to reduce the arbitrariness implicit in the choice of the parameters (*a* and φ) involved in the use of eqs 5−7 appears to be useful. A way to do this is to combine measurements of solvent shifts of both absorption and fluorescence bands. Details of this procedure can be found in the literature.[16] Briefly, from eq 5 and the corresponding equation for $\tilde{\nu}_{\rm F}$, the solvent dependent wavenumber of the fluorescence maximum, it is straightforward to get the following expressions for $\tilde{\nu}_{\rm A} + \tilde{\nu}_{\rm F}$ and $\tilde{\nu}_{\rm A} - \tilde{\nu}_{\rm F}$

$$\tilde{\nu}_{\rm A} + \tilde{\nu}_{\rm F} = -m_{\rm A+F}[f(\varepsilon) + f(n^2)] \quad \text{with} \quad m_{\rm A+F} = 2\frac{({\mu_{\rm e}}^2 - {\mu_{\rm g}}^2)}{hca^3} \tag{8}$$

$$\tilde{\nu}_{\rm A} - \tilde{\nu}_{\rm F} = m_{\rm A-F}[f(\varepsilon) - f(n^2)] \quad \text{with} \quad m_{\rm A-F} = 2\frac{(\vec{\mu}_{\rm e} - \vec{\mu}_{\rm g})^2}{hca^3} \tag{9}$$

Determination of $m_{\rm A+F}$ and $m_{\rm A-F}$ opens up new ways of obtaining the excited-state dipole moment. First of all, in terms of $m_{\rm A+F}$, $\mu_{\rm e}$ can be simply expressed as

$$\mu_{\rm e} = \left({\mu_{\rm g}}^2 + \frac{m_{\rm A+F}hca^3}{2}\right)^{1/2} \tag{10}$$

thus avoiding any specification of the angle φ. On the other hand, in terms of $m_{\rm A-F}/m_{\rm A+F}$, cos φ is given by

$$\cos\phi = \frac{1}{2\mu_{\rm g}\mu_{\rm e}}\left[({\mu_{\rm e}}^2 + {\mu_{\rm g}}^2) - \frac{m_{\rm A-F}}{m_{\rm A+F}}({\mu_{\rm e}}^2 - {\mu_{\rm g}}^2)\right] \tag{11}$$

Finally, if $\vec{\mu}_g$ and $\vec{\mu}_e$ are parallel, a case not very far from ours, $\mu_{\rm e}$ can be obtained by the expression

$$\mu_{\rm e} = \frac{m_{\rm A-F} + m_{\rm A+F}}{m_{\rm A+F} - m_{\rm A-F}}\mu_{\rm g} \tag{12}$$

which leaves aside the cavity radius.

It should be remembered that the advantages of using eqs 8−12 are partly reduced by the additional assumption that the ground- and excited-state dipole moments involved in the absorption and emission processes are the same. In other words, the $\mu_{\rm e}$ obtained in this way should be regarded as intermediate between those of the Franck−Condon absorption and fluorescence emitting excited states.

Apart from this, use of eqs 8−12 requires the molecules under study to be efficient fluorophores. Unfortunately, fluorescence emission was weak for all Mc1−4 merocyanines in all solvents. However, its intensity increased together with the chromophore length: we could not observe it for Mc1, it started to emerge from noise for Mc2, it was discernible, but mixed with impurity emissions for Mc3 and could rather well be spectrally characterized for Mc4. In particular, for the latter we found the desired independence of emission on excitation wavelength and of excitation on the emission wavelength, as well as matching between absorption and excitation spectra. Therefore, only for Mc4 could we obtain emission maxima in a choice of solvents and in n-hexane/diethyl ether binary mixtures (Supporting Information, Figure S3) to be employed in the solvatochromic analysis. As found with absorption data, in the pure solvent series data are more scattered and show a more pronounced slope (−10700 cm^{-1}) than in the binary mixture series (−5900 cm^{-1}). On this basis, in keeping with what stated in section 4.2.2.1, we will limit ourselves to consider the solvatochromic behavior of $\tilde{\nu}_{\rm A} + \tilde{\nu}_{\rm F}$ and $\tilde{\nu}_{\rm A} - \tilde{\nu}_{\rm F}$ in *n*-hexane/diethyl ether mixtures, particularly in the lowest-polarity binary mixtures.

Detailed plots of $\tilde{\nu}_{\rm A} + \tilde{\nu}_{\rm F}$ versus $[f(\varepsilon) + f(n^2)]$ and $\tilde{\nu}_{\rm A} - \tilde{\nu}_{\rm F}$ versus $[f(\varepsilon) - f(n^2)]$ are given in the Figures S4 and S5 (Supporting Information). In short, linear regression of the $\tilde{\nu}_{\rm A} + \tilde{\nu}_{\rm F}$ values in the four lowest-polarity binary mixtures led to $m_{\rm A+F} \cong 10600$ cm^{-1} with an almost unitary correlation coefficient. Substitution in eq 10, together with $a = 3.67$ Å and $\mu_{\rm g} = 6.61$ D, gives $\mu_{\rm e} = 9.78$ D (and $\Delta\mu_{\rm eg} = 3.17$ D), in reasonably good agreement with $\mu_{\rm e} = 10.38$ D ($\Delta\mu_{\rm eg} = 3.77$ D) obtained for Mc4 in section 4.2.2.1 using eq 7 with $m_{\rm A} = 4713$ cm^{-1} (Figure 6 and Table 6). As to $m_{\rm A-F}$, the situation is much less favorable in view of the strong dispersion of the $\tilde{\nu}_{\rm A} - \tilde{\nu}_{\rm F}$ values (Supporting Information, Figure S5). So, $m_{\rm A-F}$ can only be given with a rather large margin of error, $m_{\rm A-F} = 1500 \pm 300$ cm^{-1}.

By substitution in eq 11 with $m_{\rm A+F} = 10600$ cm^{-1}, $\mu_{\rm e} = 9.78$ D and $\mu_{\rm g} = 6.61$ D, we obtain a cos φ value very close to 1 (the actual numerical value being 1.016 ± 0.011). This result indicates substantial parallelism of $\vec{\mu}_{\rm e}$ and $\vec{\mu}_{\rm g}$ in Mc4, in qualitatively good agreement with quantum mechanical calculations predicting φ to be about 10° in the longest both trans and cis merocyanine. Finally, with the assumption that ground- and excited-state dipole moments are parallel, we can use eq 12 to estimate $\mu_{\rm e}$. Using $\mu_{\rm g} = 6.61$ D, $m_{\rm A+F} = 10600$ cm^{-1} and $m_{\rm A-F} = 1500 \pm 300$ cm^{-1}, eq 12 gives $8.30 < \mu_{\rm e} < 9.30$ D, which is not very far from $\mu_{\rm e} = 9.78$ D obtained by eq 10. To conclude, within the rather low accuracy limits in the determination of $m_{\rm A-F}$, application of eqs 10−12 has provided an at least qualitative validation of procedure 2 used in section 4.2.2.1 to determine μ_e, and hence $\Delta\mu_{eg}$ and β_{XXX}, for Mc1−4 merocyanines.

5. Conclusions

Most reported studies concerning the first hyperpolarizability of D−π−A chromophores refer to the so-called two-level (or two-state) model, having its grounds in the SOS theoretical scheme, as a simple tool capable of providing qualitative indications in the search for new promising second-order NLO compounds. However, there exist donor−acceptor systems for which the two-level model may in principle account for hyperpolarizability β in a quasi-quantitative way. With reference to the SOS scheme, this requires the absence of excited states with appreciable values of both μ_{ge} and $\Delta\mu_{eg}$ in the proximity of the lowest lying CT $^1(\pi\pi^*)$ state characterizing such systems. In this respect, on the basis of spectroscopic evidence, streptomerocyanines appear to be suitable model D−A chromophores. In this work, the two-level model has been thoroughly tested both experimentally and theoretically for four merocyanines Mc1−4 bearing a $-C(CH_3)O$ electron-acceptor group (Chart 2). The focus was on the "free-molecule" first- and second-order polarizabilities and their dependence on the length of the conjugation path.

Molecular structures were first investigated by ^{1}H NMR spectroscopy and quantum mechanical both semiempirical and ab initio calculations. At ordinary T, solutions of Mc1−4 were found to be ~1:1 mixtures of conformers with trans and cis arrangements of the $-C(CH_3)O$ group and all trans structure of the polyenic bridge. From full geometry optimization at the DFT(6-31G**/B3LYP) level both isomers were confirmed to be planar with all trans polyene fragments characterized by a BLA ≅ 0.07 Å. Ground-state dipole moments of the solution 1:1 trans/cis mixtures were estimated from literature data in $CHCl_3$ for trans streptomerocyanines with $n = 1, 2, 3$ and the ratio $\langle \mu_g^{cis}/\mu_g^{trans} \rangle \cong 0.8$ predicted by theory.

The experimental two-level-model determination of the dominant components of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ tensors was designed to approximate the isolated-molecule values. As regards α_{XX} this was obtained by simply measuring the CT transition properties (E_{ge} and μ_{ge}) in an apolar solvent. On the other hand, for the solvatochromic method, adopted to determine the difference between excited- and ground-state dipole moment $\Delta\mu_{eg}$ entering the expression of β_{XXX}, we had to devise a special approach. This was based on the determination of the solvatochromic slopes by accurate solvent-shift measurements of the absorption maxima in a few n-hexane/diethyl ether mixtures with small diethyl ether volume fractions. Qualitatively speaking (only four data points being used), the so obtained first- and second-order polarizabilities of merocyanines Mc1−4 were found to rise with n according to the relationships $\alpha_{XX} \propto n^{1..3}$ and $\beta_{XXX} \propto n^{2.1}$, respectively. The β_{XXX}'s determined by our optimized solvatochromic procedure fit very well those obtained by Marder et al. by EFISH measurements in $CHCl_3$ for three streptomerocyanines with $n = 1, 2, 3$. For the longest-chain chromophore (Mc4), the only one with intense enough fluorescence, the $\Delta\mu_{eg}$ derived from the absorption solvent shifts was satisfactorily reproduced using solvent shifts of both absorption and fluorescence bands. An experimental, at least qualitative, validation of the two-level model α_{XX}'s was also obtained by reference to $\langle\alpha\rangle$ values from molar refraction measurements reported for two streptomerocyanines corresponding to Mc1 and Mc2.

Starting from the DFT-optimized ground-state geometries, the CT excited-state properties (E_{ge}, μ_{ge}, $\Delta\mu_{eg}$) entering the two-level model expressions of α_{XX}, β_{XXX} were calculated for trans and cis Mc1−4 at the semiempirical SCF-CI level by ZINDO/S (using Mataga−Nishimoto repulsion integrals and SCI) and CS INDO (using Ohno−Klopman integrals and both SCI and SDCI) methods. Not unexpectedly, calculated α_{XX}'s and β_{XXX}'s were found to be not very sensitive to the trans or cis arrangement of the acceptor group. Apart from their absolute values, the α_{XX}'s and β_{XXX}'s obtained by the three theoretical approaches rise with n following approximately the same relationships as the experimental two-level model values: $\alpha_{XX} \propto n^{1.3}$, $\beta_{XXX} \propto n^2$. As to the absolute values, however, the performances of the three approaches were rather different. Thanks above all to inclusion of doubly excited configurations leading to satisfactory predictions of the transition dipole moments, two-level model CS INDO SDCI calculations provided the best values of both α_{XX} and β_{XXX}. Experimental two-level model data obtained here for Mc1−4 were reproduced quite well at the CS INDO SDCI level of calculation. Converged SOS calculations were found to fit well two-level model calculations, especially those using SCI. In keeping with the SOS results, finite field INDO calculations of Mc1−4 α_{XX} 's provided values consistent with those obtained by the two-level model CS INDO approach, the divergence being most likely due to the different formulations of the INDO Hamiltonian.

To sum up, it has been shown that as far as simple merocyanines are concerned both individual absolute values and dependence on the conjugation path length of first- and second-order molecular polarizabilities in neutral medium can be rather accurately accounted for within the two level model. With reference to the general SOS scheme, a detailed experimental and theoretical analysis of the electronic spectrum may be revealing about the applicability of the two level model to more complex D−π−A systems.

Acknowledgment. Dr. M. Cecilia Rossi of CIGS (University of Modena and Reggio Emilia) is warmly thanked for carrying out the NMR experiments. Useful discussions on dipole moments with Dr. Francesca Tessore (University of Milan) are gratefully acknowledged.

Supporting Information Available: Tables of geometries, dipole moments, optical properties, and polarizabilities. Figures of absorption wavenumbers, emission wavenumbers, and $\tilde{\nu}_A^{max} \pm \tilde{\nu}_F^{max}$. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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

(2) Optical Nonlinearities in Chemistry. Special issue of *Chem. Rev.* 1994, *94*, No. 1.

(3) Morley, J. O.; Hutchings, M. G.; Zyss, J.; Ledoux, I. *J. Chem. Soc., Perkin Trans.* **1997**, *2*, 1139.

(4) Hrobarik, P.; Zahradnik, P.; Fabian, M. F. *Phys. Chem. Chem. Phys.* **2004**, *6*, 495.

(5) (a) Baraldi, I.; Ghelli, S.; Krasnaya, Z. A.; Momicchioli, F.; Tatikolov, A. S.; Vanossi, D.; Ponterini, G. *J. Photochem. Photobiol. A: Chem.* **1997**, *105*, 297. (b) Baraldi, I.; Momicchioli, F.; Ponterini, G.; Tatikolov, A. S.; Vanossi, D. *Phys. Chem. Chem. Phys.* **2003**, *5*, 979.

(6) (a) Baraldi, I.; Momicchioli, F.; Ponterini, G.; Vanossi, D. *Chem. Phys.* **1998**, *238*, 353. (b) Baraldi, I.; Momicchioli, F.; Ponterini, G.; Vanossi, D. *Adv. Quantum Chem.* **1999**, *36*, 121. (c) Baraldi, I.; Brancolini, G.; Momicchioli, F.; Ponterini, G.; Vanossi, D. *Chem. Phys.* **2003**, *288*, 309.

(7) Reichardt, C. *Solvent Effects in Organic Chemistry*; Verlag Chemie: Weinheim, 1979.

(8) Amos, A. T.; Burrows, B. L. *Adv. Quantum Chem.* **1973**, *7*, 289.

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

(10) Meyers, F.; Marder, S. R.; Pierce, B. M.; Brédas, J. L. *J. Am. Chem. Soc.* **1994**, *116*, 10703.

(11) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Phys. Chem.* **1996**, *100*, 9714.

(12) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Brédas, J.-L.; Pierce, B. M. *Science* **1994**, *265*, 632.

(13) Marder, S. R.; Gorman, C. B.; Tiemann, B. G.; Cheng, L.-T. *J. Am. Chem. Soc.* **1993**, *115*, 3006.

(14) Bourhill, G.; Brédas, J.-L.; Cheng, L.-T.; Marder, S. R.; Meyers, F.; Perry, J. W.; Tiemann, B. G. *J. Am. Chem. Soc.* **1994**, *116*, 2619.

(15) Ward, J. *Rev. Mod. Phys.* **1965**, *37*, 1.

(16) Kawski, A. *Z. Naturforsch.* **2002**, *57a*, 255.

(17) DeMartino, R. N.; Choe, E. W.; Khanarian, G.; Haas, D.; Leslie, T.; Nelson, G.; Stamatoff, J.; Stutz, D.; Teng, C. C.; Yoon, H. In *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., Ulrich, D. R., Eds.; Plenum: New York, 1988, pp 169−187.

(18) Paley, M. S.; Harris, J. M.; Looser, H.; Baumert, J. C.; Bjorklund, G. C.; Jundt, D.; Twieg, R. J. *J. Org. Chem.* **1989**, *54*, 3774.

(19) McLean, M. R.; Bader, M.; Dalton, L. R.; Devine, R. L. S.; Steier, W. H. *J. Phys. Chem.* **1990**, *94*, 4386.

(20) Sworacowski, J.; Lipiński, J.; Ziólek, L.; Palewska, K.; Nešpùrek, S. *J. Phys. Chem.* **1996**, *100*, 12288.

(21) Kucharski, S.; Janik, R.; Kaatz, P. *J. Phys. Chem. B* **1997**, *101*, 8967.

(22) Chou, S.-S. P.; Hsu, G.-T.; Lin, H.-C. *Tetrahedron Lett.* **1999**, *40*, 2157.

(23) Bruni, S.; Cariati, E.; Cariati, F.; Porta, F. A.; Quici, S.; Roberto, D. *Spectrochim. Acta A* **2001**, *57*, 1417.

(24) Pan, Q.; Fang, C.; Zhang, Z.; Qin, Z.; Li, F.; Gu, Q.; Wu, X.; Yu, J. *Opt. Mater.* **2003**, *22*, 45.

(25) Huang, X.; Zhong, S.; Yan, X.; Ke, X.; Srisanit, N.; Wang, M. R. *Synth. Met.* **2004**, *140*, 79.

(26) Qian, Y.; Lin, B.; Xiao, G.; Li, H.; Yuan, C. *Opt. Mater.* **2004**, *27*, 125.

(27) Chen, L.; Cui, Y.; Mei, X.; Qian, G.; Wang, M. *Dyes Pigments* **2007**, *72*, 293.

(28) It should be noted, for example, that in ref 12 hyperpolarizabilities calculated for the streptomerocyanine with $n = 4$ were discussed in terms of EFISH measurements carried out for merocyanines with $n = 3$.

(29) Dähne, S.; Nolte, K.-D. *J. Chem. Soc., Chem. Commun.* **1972**, 1056.

(30) Ridley, J. E.; Zerner, M. C. *Theor. Chim. Acta* **1973**, *32*, 111. **1976**, *42*, 223.

(31) Momicchioli, F.; Baraldi, I.; Bruni, M. C. *Chem. Phys.* **1983**, *82*, 229.

(32) (a) Ohno, K. *Theor. Chim. Acta* **1964**, *2*, 219. (b) Klopman, G. *J. Am. Chem. Soc.* **1964**, *86*, 4550.

(33) HyperChem, *Computational Chemistry Manual*, Hypercube, Inc.: 2002.

(34) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E. et al. *Gaussian 03*, revision B.04; Gaussian, Inc.: Pittsburgh, PA, 2003.

(35) Momicchioli, F.; Baraldi, I.; Carnevali, A.; Ponterini, G. In *Strategies and Applications in Quantum Chemistry*; Ellinger, Y., Defranceschi, M., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996; p 379.

(36) Mataga, N.; Nishimoto, K. *Z. Phys. Chem.* **1957**, *12*, 335; *13*, 140.

(37) Radeglia, S.; Dähne, S. *J. Mol. Struct.* **1970**, *5*, 399.

(38) Scheibe, G.; Sciffert, W.; Hohlneicher, G.; Jutz, Ch.; Springer, H. J. *Tetrahedron Lett.* **1966**, *41*, 5053.

(39) Radeglia, R.; Gey, E.; Steiger, Th.; Kulpe, S.; Lück, R.; Ruthenberg, M.; Stierl, M.; Dähne, S. *J. Prak. Chem.* **1974**, *316*, 766.

(40) A secondary series of signals was also observed for both compounds, though especially for Mc4, in benzene. In the case of Mc4, these signals were assigned to a long-lived photoisomer obtained by twisting about the C_3-C_4 bond, as suggested by the observation of a strong NOE between H_2 and H_5 (at 8.04 and 6.68 ppm, respectively) and their decrease with time if kept in the dark (the signal intensities roughly halved in a couple of weeks). UV−vis spectroscopic measurements (see section 4.2.1) were therefore performed taking care to minimize the exposure of the samples to ambient light.

(41) Merocyanines can be regarded as either donor-acceptor polyenes[10] or unsymmetrical polymethine-cyanines.[42] The BLA definition adopted here refers to the first viewpoint stressing the BLA reduction induced by D and A substituents on the parent polyene. The BLA definition based on the second view-point, previously adopted by us,[6a,b] stresses on the contrary the loss of bond uniformity relative to the parent symmetrical cyanine.

(42) Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants*; Springer: Berlin, 1980; Chapter 12.

(43) Kushitsu, K.; Fukuyama, T.; Morino, Y. *J. Mol. Struct.* **1969**, *4*, 41.

(44) Marder, S. T.; Perry, J. W.; Tiemann, B. G.; Gorman, C. B.; Gilmour, S.; Biddle, S. L.; Bourhill, G. *J. Am. Chem. Soc.* **1993**, *115*, 2524.

(45) Baughman, R. H.; Kohler, B. E.; Levy, I. J.; Spangler, C. *Synth. Met.* **1985**, *11*, 37.

(46) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643.

(47) Lippert, E. *Ber. Bunsenges. Phys. Chem.* **1957**, *61*, 962.

(48) Bodor, N.; Gabanyi, Z.; Wong, C. *J. Am. Chem. Soc.* **1989**, *111*, 3783.

(49) Kamlet, M. J.; Abboud, J. L.; Taft, R. W. *J. Am. Chem. Soc.* **1977**, *99*, 6027.

(50) Baumann, W.; Nagy, Z. *Pure Appl. Chem.* **1993**, *65*, 1729.

(51) Of course, the tight correspondence with the EFISH $\beta(0)$'s in $CHCl_3$ should be considered with due caution, in view of the slight difference between the studied merocyanines as well as the occurrence of a conformational equilibrium in our samples.

(52) Barzoukas, M.; Blanchard-Desce, M.; Josse, D.; Lehn, J.-M.; Ziss, J. *Chem. Phys.* **1989**, *133*, 323.

JP8080854