[*n*]-Polyenovanillins (*n* = 1−6) as New Push−Pull Polyenes for Nonlinear Optics: Synthesis, Structural Studies, and Experimental and Theoretical Investigation of Their Spectroscopic Properties, Electronic Structures, and Quadratic Hyperpolarizabilities

Thierry Brotin,[†] Chantal Andraud,*[,†] Isabelle Ledoux,[‡] Sophie Brasselet,[‡] Joseph Zyss,[‡] Monique Perrin,[§] Alain Thozet,[§] and André Collet*[,†]

École normale supérieure de Lyon, Stéréochimie et Interactions moléculaires, 69364 Lyon cedex 07, France; Centre National d'Étude des Télécommunications, France Télécom, Bagneux, France; and Université Claude Bernard, Laboratoire de Cristallographie, 69622 Villeurbanne cedex, France

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We describe the synthesis and quadratic hyperpolarizability properties of [*n*]-polyenovanillins, a new family of push−pull polyenes deriving from vanillin, thiovanillin, and isothiovanillin. Twenty-five [*n*]-polyenovanillins of structure 3,4-(RO;R′S)C_6H_4(CH═CH)$_n$-CH═O [with *n* = 1−6 and R, R′ = Me or *n*-Bu] were synthesized by using a Wittig−Horner polyvinylogation methodology, and the structure of one of these was established by single-crystal X-ray crystallography. The UV−vis absorption and fluorescence spectra of these polyenovanillins were recorded and interpreted in light of CNDO/S calculations that allowed the identification of the different transitions. EFISH measurements provided β_{exp}^0 up to 350 × 10^{-30} esu (for **14**, *n* = 6) with an exponential increase of the quadratic hyperpolarizability with the conjugation length. These data were satisfactorily interpreted by means of a CNDO/S/NLO method which provided information as to the relative orientation of the dipole moment μ and β_{vec}, the vector part of the hyperpolarizability tensor. In the sulfur-substituted series, there is a significant divergence between the orientation of μ and β_{vec}, which in turn leads to an underestimation of β in the EFISH method. The calculation also revealed that when the length of the polyenic chain increases, the charge transfer from the donor toward the acceptor actually tends to concentrate on the polyenic chain rather than on the aldehyde group.

I. Introduction

Conjugated polyenes with various combinations of terminal electron donor and/or acceptor groups have been the object of a continuous interest over the past two decades, particularly in view of their large molecular hyperpolarizabilities,[1] which may lead to a wide range of applications in integrated optics (second-harmonic generation, frequency mixing, electrooptic modulation, parametric effects, etc.).[2] In addition to their interest in nonlinear optics (NLO), these systems, which may represent good models for understanding the properties of large one-dimensional π-electron networks (e.g., polyacetylene), have also been involved in different contexts, e.g., as "molecular wires", facilitating the transfer of electrons across lipid membranes,[3] or in connection with studies of electron transfer processes in the photosynthetic system.[4]

In this paper, we report the synthesis, structure, spectroscopic properties and quadratic hyperpolarizabilities of a series of 25 [*n*]-polyenovanillins (*n* = 1−6, **13**−**15** in Chart 1), a new family of push−pull polyenes deriving from vanillin (**1**), thiovanillin (**3**), and their iso derivatives **2** and **4**. In previous studies, we have examined the potential usefulness of these simple donor−acceptor building blocks for the construction of push−pull hyperpolarizable molecules.[5] A detailed investigation (based on CNDO/S calculations and EFISH measurements) of the quadratic molecular hyperpolarizabilities (β) of **1**−**4** led to the encouraging conclusion that the 4-mercapto-3-methoxyphenyl group (the donor fragment in thiovanillin **3**) could be considered as equivalent, with regard to its donor properties, to the *p*-(dimethylamino)phenyl group. Moreover, CNDO/S calculations of β in polyenovanillin models **1a**−**g** (*n* = 1−7), which are vinylogs of vanillin itself, led to the prediction that the quadratic hyperpolarizability of

[†] École normale supérieure de Lyon (UMR CNRS 117).
[‡] Centre National d'Étude des Télécommunications.
[§] Université Claude Bernard.
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(1) (a) Cheng, L.-T.; Tam, W.; Marder, S. R.; Stiegman, A. E.; Rikken, G.; Spangler, C. W. *J. Phys. Chem.* **1991**, *95*, 10643−10652. (b) Barzoukas, M.; Josse, D.; Zyss, J.; Gordon, P.; Morley, J. O. *Chem. Phys.* **1989**, *139*, 359. (c) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J.; Pucetti, G.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1993**, *115*, 860−867. (d) Samuel, I. D. W.; Ledoux, I.; Dhenaut, C.; Zyss, J.; Fox, H. H.; Schrock, R. R.; Silbey, R. J. *Science* **1994**, *265*, 1070−1072.

(2) (a) Chemla, D. S., Zyss, J., Eds. *Nonlinear Optical Properties of Organic Molecules and Crystals;* Academic Press: New York, 1987; Vol. 1−2. (b) Zyss, J. Ed. *Molecular Nonlinear Optics*; Academic Press: Boston, 1993.

(3) Blanchard-Desce, M.; Arrhenius, T. S.; Lehn, J.-M. *Bull. Soc. Chim. Fr.* **1993**, *130*, 266−272.

(4) For instance, see: Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res.* **1993**, *26*, 198−205 and references therein.

(5) Andraud, C.; Brotin, T.; Garcia, C.; Pellé, F.; Goldner, P.; Bigot, B.; Collet, A. *J. Am. Chem. Soc.* **1994**, *116*, 2094−2102.

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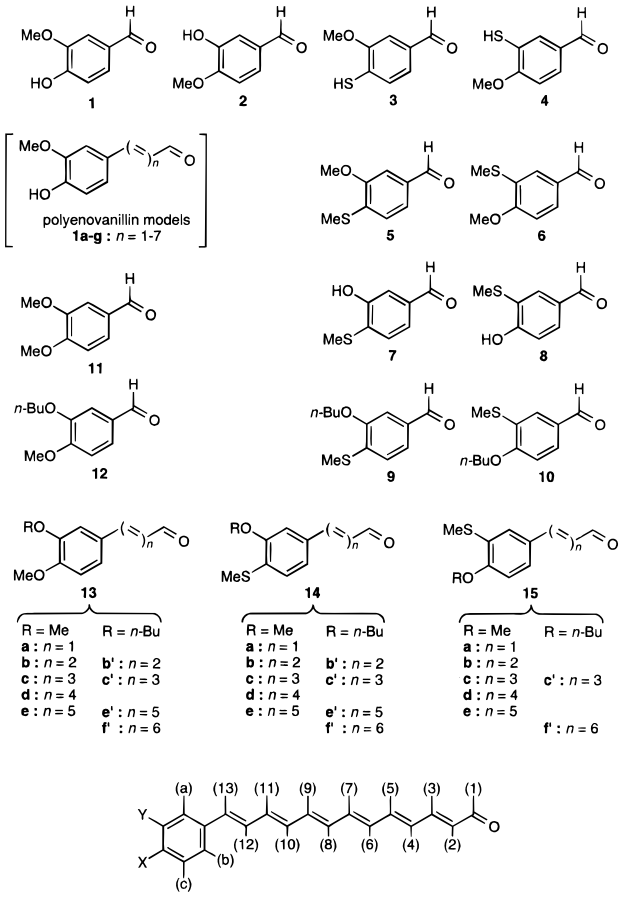
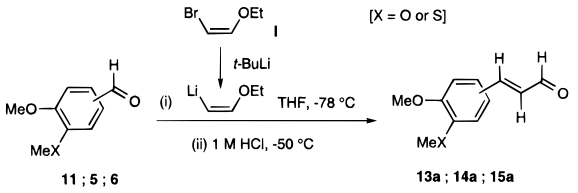
Chart 1. Structures and Atom Numbering



these compounds should increase as m^2 (where $m = n + 2$), without saturation of the hyperpolarizability density at least up to $m = 9$. The purpose of this work was to verify these predictions and to evaluate the potential interest of these new polyenes as NLO materials not only in terms of optical response but also in terms of chemical accessibility and photochemical and thermal stability.

To our knowledge, with the exception of the first member of the series (**1a**, $n = 1$, coniferyl aldehyde),[6] the synthesis of polyenovanillins of structure **1b**−**g** has not been reported. To circumvent potential synthetic problems due to the presence of a free phenol or thiophenol group, we found preferable to consider the synthesis of O- and S-alkylated derivatives, such as the [*n*]-polyenovanillins **13**−**15**. Among these compounds, only the synthesis of polyenes **13a**−**d** (the O-methylated derivatives of **1a**−**d**) had previously been described by Makin et al.[7] In section II we describe the methodology we employed for the synthesis of these polyenes, and we show that they can be reached in one ($n = 1-3$) or two ($n = 4-6$) steps from the appropriate aldehydes **5**, **6**, and **9**−**12**. A detailed NMR study of these molecules is presented in section III, evidencing the all-trans configuration of their polyenic chain. In section IV we describe the X-ray crystal structure of **15c** and address the question of the bond alternation and conformational behavior of these molecules in light of molecular mechanics and quantum calculations.

Chart 2. Synthesis of 13a, 14a, and 15a



In section V, we present experimental data and theoretical considerations concerning the absorption and fluorescence spectra, and the solvatochromism of **13**−**15**. In section VI, we report the results of EFISH measurements of β for these molecules. Finally, section VII is devoted to a general discussion of the relationships between electronic structure, conformational behavior, and nonlinear optical properties of these polyenes. We address, in relation with solvatochromism measurements and CNDO/S calculations, the question of the extent of charge transfer (CT) occurring within the polyenic chain. A significant finding is the observation that when the conjugation length increases, the electron density of the CT state tends to concentrate on the chain itself rather than on the acceptor group. As a consequence of this phenomenon, the difference in efficiency between the donors in series **13**−**15** decreases when the chain length increases.

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

II. Synthesis of Polyenovanillins 13−15

Polyenovanillins **13**−**15** were prepared by vinylogation or polyvinylogation of the 3,4-disubstituted benzaldehydes **5**, **6**, **11** and **9**, **10**, **12**. Aldehydes **5** and **6** were obtained from thiovanillin **3** and isothiovanillin **4** as described in a previous paper.[8] On reaction with boron tribromide in dichloromethane, **5** and **6** gave the corresponding phenols **7** and **8** in ca. 60% yield; these phenols on alkylation with 1-bromobutane (K_2CO_3, DMF, 80 °C, ca. 90%) were converted to the (MeS, BuO)-substituted benzaldehydes **9** and **10**. Aldehyde **12** was similarly prepared by reaction of isovanillin **2** with 1-bromobutane.

The cinnamaldehyde derivatives **13a**, **14a**, and **15a** were prepared by reaction of the corresponding benzaldehydes (Chart 2) with (*Z*)-1-lithio-2-ethoxyethylene (generated from (*Z*)-1-bromo-2-ethoxyethylene **I** and 2 equiv of *t*-BuLi)[9] in THF at −78 °C. The desired

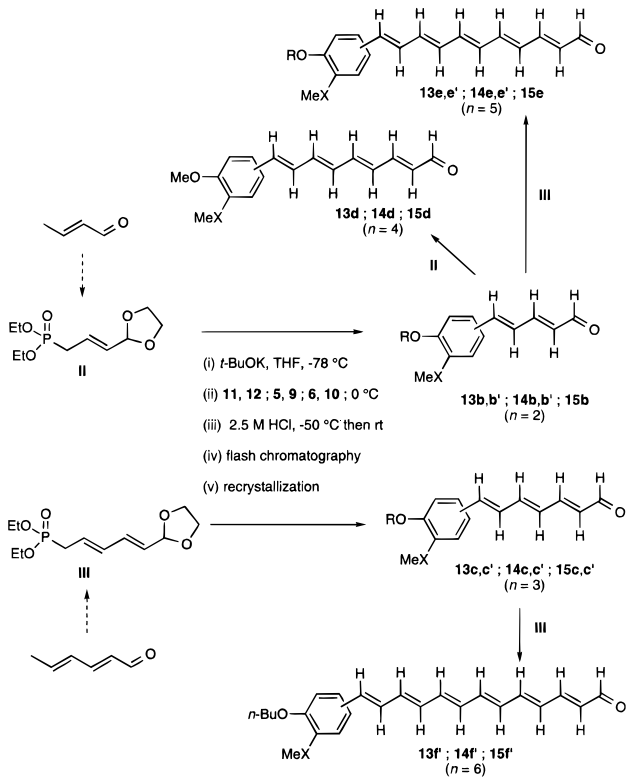
(6) Daubresse, N.; Francesh, C.; Mhamdi, F.; Rolando, C. *Synthesis* **1994**, 369−371 and references therein.

(7) Makin, S. M.; Shavrygina, O. A.; Dobretsova, E. K.; Ermakova, G. A.; Dymshakova, G. M. *Zh. Org. Khim.* **1982**, *18*, 749−755.

(8) Garcia, C.; Andraud, C.; Collet, A. *Supramol. Chem.* **1992**, *1*, 31−45.

(9) (a) Wollenberg, R. H.; Albizati, K. F.; Peries, R. *J. Am. Chem. Soc.* **1977**, *99*, 7365−7367. (b) Wollenberg, R. H. *Tetrahedron Lett.* **1978**, *8*, 717−720. (c) Law, K. S. Y.; Schlosser, M. *J. Org. Chem.*, **1978**, *43*, 1595−1598. (c) The corresponding O-silylated compound can also be used. See, for example: Duhamel, L.; Tombret, F. *J. Org. Chem.* **1981**, *46*, 3741−3742.

Chart 3. Synthesis of 13b−f′, 14b−f′, and 15b−f′



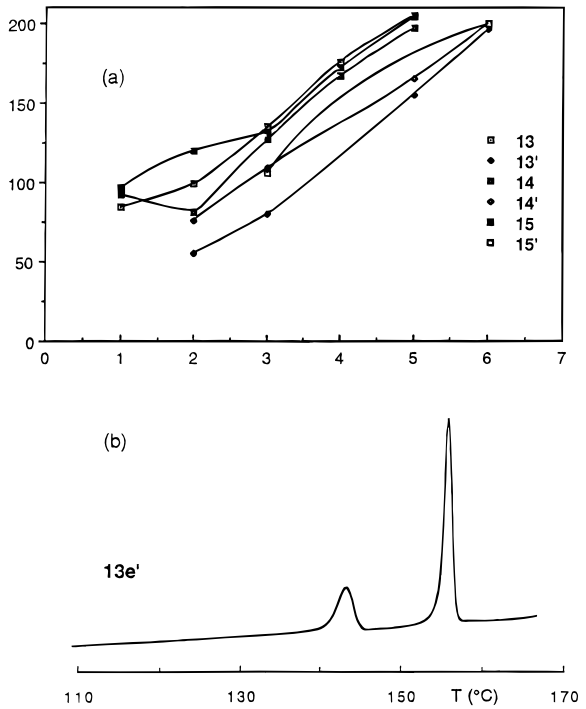


Figure 1. (a) Melting points (°C) of polyenovanillins **13**−**15** and (b) DSC record of **13e′** at 5 K/min showing the existence of a solid−solid phase transition prior to melting.

compounds were isolated in ca. 60−80% yield after purification by flash chromatography.

The higher polyenals were synthesized by a Wittig−Horner procedure using the phosphonate reagents **II** and **III**, recently developped by Duhamel et al.[10] for the bis and trisvinylogation of aldehydes in a single step (Chart 3). Phosphonates **II** and **III** were prepared in three and four steps, respectively, from crotonaldehyde and sorbaldehyde.[11]

For the preparation of the [2]- and [3]-polyenovanillins **13**−**15b**,**b′** and **c**,**c′**, the phosphonate **II** (or **III**) was first deprotonated by *t*-BuOK (-78 °C, THF) and then allowed to react with the appropriate aldehyde at −78 to 0 °C (Chart 3). After hydrolysis (2.5 M HCl, −50 °C) a mixture of stereoisomers was obtained which could be equilibrated to the pure all-trans isomer in the presence of a catalytic amount of iodine in dichloromethane (room temperature, daylight); the desired compound was isolated by flash chromatography and eventually recrystallized.

The longest [4]−[6]-polyenovanillins were similarly obtained by reaction of the preceding [2]- and [3]-polyenals **13**−**15b**,**b′** and **c**,**c′** with either **II** or **III**. The crude reaction product consisted of ca. 90% of all-trans isomer in all cases (from NMR measurements), and the undesired stereoisomers were eliminated by flash chromatography and recrystallization from dichloromethane or from mixtures of dichloromethane and pentane. For solubility reasons,[12] only the [6]-polyenovanillins **13**−**15f′** with *n*-butoxy instead of methoxy substituents were prepared.[13]

The purity and thermal stability of these polyenals was checked by differential scanning calorimetry (DSC). There is an average mp increase of ca. 25 °C per additional double bond, and the replacement of a methoxy by a butoxy substituent lowers the melting point by ca. 50 °C in **13** and 5−30 °C in **14** and **15** (Figure 1). All compounds showed sharp melting peaks (high purity) and melted without decomposition, except the [5]- and [6]-polyenals **13**−**15e** and **13**−**15f′** which decomposed at 195−205 °C. Some of these compounds exhibited several solid-solid phase transitions before melting (for an example, see Figure 1).

III. NMR Studies of 13−15

The structure and stereochemistry of polyenals **13**−**15** were studied by ^{1}H NMR spectroscopy using phase-sensitive COSY DQF and 2D-J resolved sequences. At 500 MHz, these two sequences allowed the identification of all the protons of the polyenic chains and the determination of the coupling constants $J_{CH=CH}$ (15−

(10) Duhamel, L.; Guillemont, J.; Le Gallic, Y.; Plé, G.; Poirier, J. M.; Ramondec, Y.; Chabardes, P. *Tetrahedron Lett.* **1990**, *31*, 3129−3132.

(11) (a) See ref 9. (b) See also: Ramondenc, Y. Thesis, Université de Rouen, 1992. Le Gallic, Y. Thesis, Universié de Rouen, 1992. (c) A wide range of synthetic precursors give also access to polyenals compounds. See, for example: Shi, L.; Xia, W.; Yang, J.; Wen, X.; Huang, Y. Z. *Tetrahedron Lett.* **1987**, *28*, 2155−2158. Duhamel, L.; Plé, G.; Ramondenc, Y. *Tetrahedron Lett.* **1989**, *30*, 7377−7380. Kann, N.; Rein, T.; Akermark, B.; Helquist, P. *J. Org. Chem.* **1990**, *55*, 5312−5323. Mukaiyama, T.; Ishida, A. *Chem. Lett.* **1975**, 319−322; **1975**, 1201−1202. Hemming, K.; Taylor, R. J. K. *J. Chem. Soc., Chem. Commun.* **1993**, 1409−1410. Contreras, B.; Duhamel, L.; Plé, G. *Synth. Commun.* **1990**, *20*, 2983−2990. See also ref 6.

(12) The introduction of a phenyl group at the end of a polyenic chain stabilizes the molecule but strongly decreases its solubility. According to Marshall et al., each additional double bond added to the *p*-methoxyphenyl moiety decreases the solubility by a factor of 8. Marshall, D.; Whiting, M. C. *J. Chem. Soc.* **1956**, *4*, 4082−4088.

(13) Although the introduction of a S−*n*-Bu substituent in series **14**−**15** may require less synthetic steps than that of a O−*n*-Bu group, the latter was preferred in this case since it has been shown that the electron acceptor character of a S−R group is enhanced with the size of the aliphatic substituent. See: Alberti, A.; Martelli, G.; Pedulli, G. F. *J. Chem. Soc., Perkins Trans. 2* **1977**, 1252−1255. Alberti, A.; Guerra, M.; Martelli, G.; Bernardi, F.; Mangini, A.; Pedulli, G. F. *J. Am. Chem. Soc.* **1979**, *101*, 4627−4631.

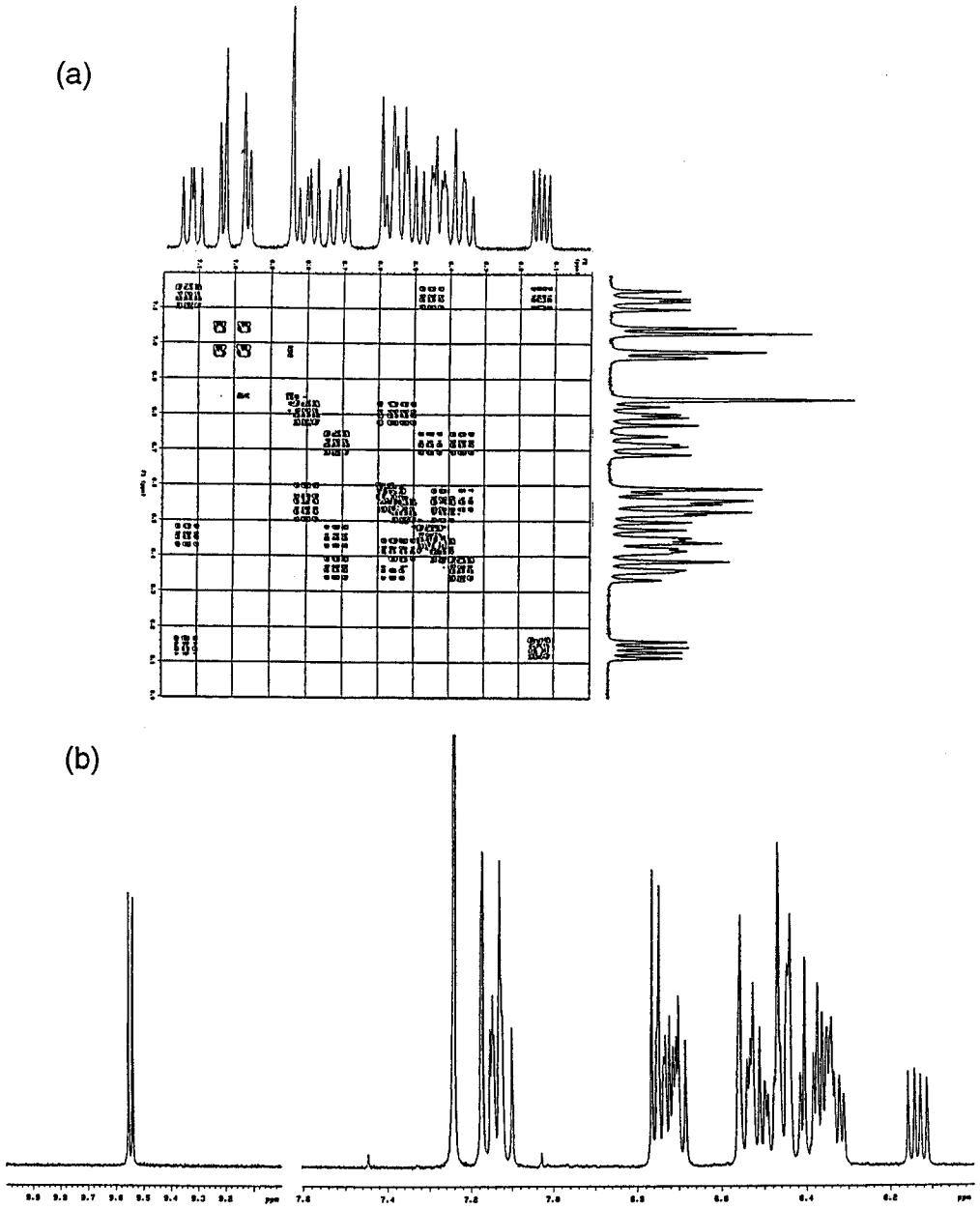


Figure 2. ^{1}H NMR spectra of polyenovanillins in $CDCl_3$ (500 MHz): (a) COSY DQF phase-sensitive spectrum of **13e′**; (b) 1D spectrum of **15f′**.

15.5 Hz) and J_{CH-CH} (11−11.5 Hz) characteristic of the all-trans structure (see Figure 2 for an example). As was already noticed,[14] odd-row protons are always downfield shifted with respect to their even-row counterparts (e.g., δ H(5) 6.72 vs H(4) 6.44 in pentaenal **13e′**). The stereochemical homogeneity of all compounds was evidenced by the presence of a single doublet at 9.6 ppm corresponding to the aldehyde proton H(1). For the [6]-polyenovanillins, a COSY DQF sequence allowed us to locate the protons of the polyenic chain, but we could not achieve the determination of all their coupling constants. There is little doubt, however, on the all-trans structure of these compounds, which is entirely consistent with the UV−vis absorption spectra reported below.

The stability of these [*n*]-polyenovanillins was found to be excellent in the solid state; samples stored at −20 °C for 1 year did not show any change in their melting points or spectroscopic properties. In contrast, these compounds proved sensitive to isomerization in solution when exposed to light. In the case of hexaenal **15f′**, we observed after 24-h exposure to daylight the presence of several doublets in the H(1) region of the NMR spectrum (9−10.5 ppm), indicating the formation of stereoisomers. When the same solution was kept in the dark almost no isomerization occurred (ca. 1% after 2 days at room temperature).

IV. Structure and Conformations of Polyenovanillins

The molecular structure of **15c** was determined by single-crystal X-ray crystallography (see Experimental Section). It is interesting that **15c** crystallizes in the noncentrosymmetric space group $P2_1$ and thus may exhibit second harmonic generation properties in the solid state. The essential features of this structure (Figure 3 and Table 1) are the following: (i) the polyenic

(14) Plé, G.; Ramondenc, Y. *New J. Chem.* **1992**, **16**, 789−790.

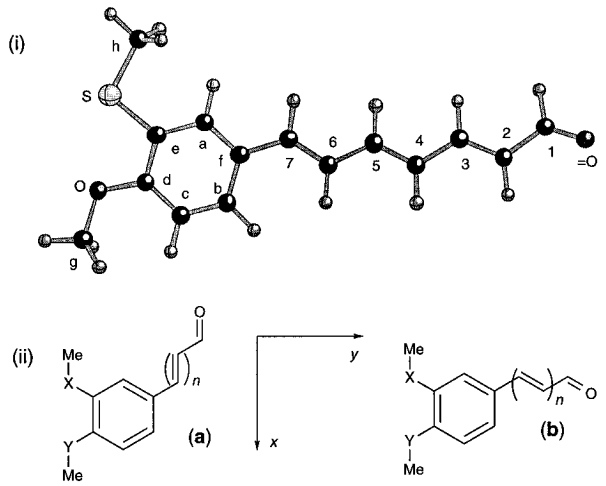


Figure 3. (i) Structure of **15c** in the solid state; (ii) conformations **a** and **b** of polyenovanillins and coordinate system for CNDO/S calculations.

Table 1. Experimental and Calculated Torsion Angles (deg), Bond Lengths (Å), and Bond Alternation (BA, in Å) in Conformations a and b of 15c[a]

		X-ray	MMX	MM^+	Tripos	AM1	PM3
a−e−S−h	**b**	−6.3	−96	0	−95	0	−27
	a		−96	−1	−95	−2	−27
c−d−O−g	**b**	1.0	−2	3	2	3	2
	a		−2	3	3	3	3
b−f−7−6	**b**	−13.7	10	0	−24	0	−4
	a		−167	180	−156	0	179
8−7	**b**/**a**	1.452	1.474	1.349	1.517	1.451	1.457
7=6	**b**/**a**	1.340	1.359	1.346	1.341	1.346	1.344
6−5	**b**/**a**	1.446	1.464	1.346	1.480	1.445	1.448
5=4	**b**/**a**	1.335	1.361	1.345	1.340	1.347	1.343
4−3	**b**/**a**	1.448	1.462	1.345	1.479	1.445	1.450
3=2	**b**/**a**	1.350	1.361	1.345	1.339	1.343	1.341
2−1	**b**/**a**	1.462	1.469	1.356	1.475	1.467	1.478
1=O	**b**/**a**	1.184	1.220	1.209	1.220	1.233	1.211
BA		0.11	0.11	0.00	0.15	0.11	0.12

[a] See Figure 3 for atom numbering.

chain and the terminal aldehyde group display an almost planar zigzag conformation, the main axis of the chain being practically opposite in direction to the Ar−O bond of the *p*-methoxy substituent; (ii) the MeO and MeS groups are almost coplanar to the benzene ring (torsion angles of 1° and 6.3°, respectively); (iii) the torsion angle b−f−7−6 between the aromatic ring and the plane of the polyenic chain is ca. 14°, a small value which allows electron transfer between the donor and acceptor ends of the molecule; (iv) the bond alternation within the polyenic chain (the difference between the average length of the single and double bonds) is 0.11 Å, a figure comparable with that observed in similar polyenes.[15]

We attempted, by molecular modeling techniques, to reproduce the solid-state geometry of **15c** and to gain information about its conformational properties in solution.[16] Disregarding the conformations of the MeO and MeS groups, there are two main conformers, **a** and **b**, which differ in the orientation of the polyenic chain with respect to the meta substituent of the aromatic ring (see Figure 3). These conformers can be conveniently differentiated by the magnitude of the torsion angle b−f−7−6, which is close to 180° in **a** and to 0° in **b**. In **15c**, as well as in the other members of the three series, these two conformers are in fact very close in energy and hence should be equally populated in solution, whereas in the solid state only conformer **b** is observed.

Molecular mechanics simulations, using the MMX and Tripos force fields, failed to reproduce the solid state conformation of the MeS group in **15c**, which, in both cases, was found almost perpendicular to the benzene ring after energy minimization (Table 1); this result may be due to an incorrect parametrization of C−S−Ar groups.[17] Both MMX and Tripos gave acceptable values of the dihedral angle b−f−7−6; however, the geometry of the polyenic chain (particularly the bond alternation) was better reproduced by the former. In contrast, the MM^+ force field gave the correct planar geometry for the MeS and MeO substituents but failed to reproduce the observed bond alternation in the polyenic chain; this force field, which yielded the polyenic chain strictly coplanar with the aromatic ring, seems to overestimate the contribution of the π-conjugation with respect to the steric requirements of the molecule. The best simulations were obtained by semiempirical quantum methods. Using AM1, the geometry of **15c** was predicted to be essentially planar while PM3 yielded a torsion angle of ca. 4° between the chain and the benzene ring (compared to 14° in the X-ray structure) and a MeS group slightly more twisted (26°) than it is in the solid state (6°). Both AM1 and PM3 accurately reproduced the observed bond alternation of the polyenic chain. In view of these results, the CNDO/S calculations of the electronic spectra and quadratic hyperpolarizabilities reported below for the interpretation of the relevant experimental properties of **13**−**15** were performed by using geometries generated by the PM3 method, the OMe or SMe substituents being eventually set strictly coplanar to the aromatic ring to which they are bound. For both conformations **a** and **b** the coordinate system was chosen so that the benzene ring and its OMe or SMe substituents lie in the *xy* plane as shown in Figure 3.

V. Spectroscopic Properties of 13−15

Typical absorption spectra at 300 K of **13**−**15** ($n = 1$, 2, and 6) are shown in Figure 4 and quantitative data on the absorption for all compounds are assembled in Table 2. As in other all-trans polyenes, the absorption spectra consist of a main broad band (I) for which $\lambda_{abs}^{(I)}$ as a function of the conjugation length follows eq V-1[18] where ($m = n + 2$), and A, B are constants (Figure 5).[19]

$$\lambda_{abs}^{(I)} = A\sqrt{m} + B \qquad \text{(V-1)}$$

(15) Ortiz, R.; Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Cavagnero, S.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* **1994**, 2263−2264. Marder, S. R.; Perry, J. W.; Tiemann, D. G.; Gorman, C. B.; Gilmour, S.; Biddle, S. L.; Bourhill, G. *J. Am. Chem. Soc.* **1993**, *115*, 2524−2525.

(16) The following softwares and force fields were used in this work: PCMODEL, from Serena Software, P. O. Box 3076, Bloomington, IN 47402−3076 (MMX force field including Pi-calculations); Hyperchem, from Autodesk, Inc., 2320 Marinship Way, Sausalito, CA 94965-9910 (MM^+ force field and AM1 calculations); SYBYL, from Tripos, 1699 S. Hanley Road, St. Louis, MO 63144-2913. (Tripos force field and PM3 calculation included in MOPAC package).

(17) For a discussion of the conformational preferences of MeO and MeS groups, see ref 8.

(18) Jaffé, H. H.; Orchin, M. *Theory and Applications of Ultraviolet Spectroscopy*; Wiley: New York, 1962; Chapter 11. Fabian, J.; Hartmann, H. *Light Absorption of Organic Colorants*; Springer-Verlag: Berlin, 1980; Chapter VI.

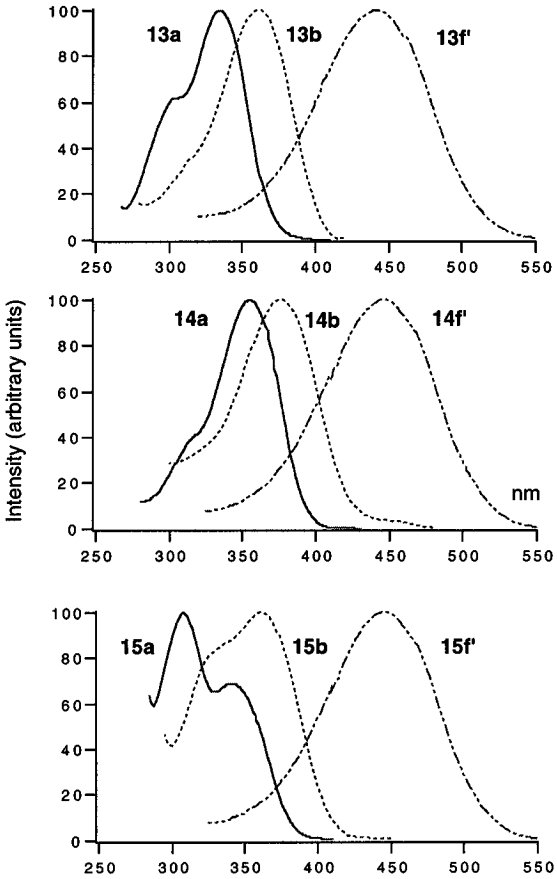


Figure 4. Normalized absorption spectra of **13**−**15** with n = 1, 2, and 6 in dichloromethane.

Table 2. Experimental Absorption and Fluorescence Data for Polyenovanillins 13−15[a]

	n	$\lambda_{abs}^{(II)}$	$\epsilon^{(II)}$	$\lambda_{abs}^{(I)}$	$\epsilon^{(I)}$	μ_{exp}
13a	1	305	14 100	335	22 500	4.0
13b	2	315sh	12 700	362	39 100	
13c	3			382	42 000	
13d	4			403	53 300	
13e′	5			425	80 000	
13f′	6			442	nd	
14a	1	305sh	14 500	355	26 500	5.5
14b	2			375	38 500	
14c	3			392	48 100	
14d	4			412	66 200	
14e′	5			427	94 400	
14f′	6			445	nd	
15a	1	308	19 000	342	13 100	5.0
15b	2	335sh	23 300	362	27 000	
15c	3			385	44 000	
15d	4			403	51 000	
15e	5			422	68 700	
15f′	6			440	98 700	

[a] See structural formulas in Chart 1; λ_{abs} (nm) is the absorption wavelength measured in CH_2Cl_2, ϵ (M^{-1} cm^{-1}) is the molar extinction coefficient; λ_f (nm) is the fluorescence wavelength measured in CH_2Cl_2; μ_{exp} (D) is the experimental ground-state dipole moment.

The smallest members (n = 1, 2) display an additional band (II) at shorter wavelength which is generally weaker than (I), except for **15a**. The presence of an additional band has already been observed in certain polyenals and considered to correspond to a $n \rightarrow \pi^*$ transition of the carbonyl group.[20] In polyenovanillins,

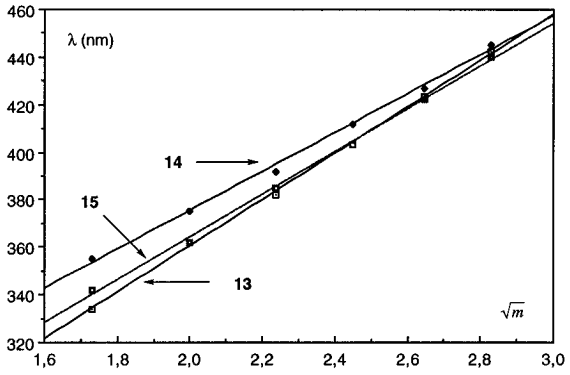


Figure 5. Plot of $\lambda_{abs}^{(I)}$ vs $\sqrt{m}$ in **13**−**15**.

this assignment was not supported by CNDO/S calculations (Table 3). For **13**−**15** (with n = 1, 2), these calculations indicated that the $n \rightarrow \pi^*$ transition of the carbonyl group was very weak and that the absorption was in fact due to a set of three $\pi \rightarrow \pi^*$ transitions **A**, **B**, and **C**. As would have been expected, the strongest transition (**A**), mainly HOMO → LUMO in character, involves principally an electron transfer from both MeO groups in **13** and from the MeS group in **14** and **15**, toward the acceptor region of the molecule (Figure 6). Transitions **B** and **C** are weaker in strength and involve also contributions of the HOMO−1 and LUMO+1 orbitals. The calculated oscillator strengths of these transitions are quite consistent with the features of the experimental spectra, which in all cases could be satisfactorily fitted in three bands as indicated in Table 3. These calculations also showed that the oscillator strength of transition **A** increases linearly with the chain length whereas only weak variations were predicted for those of **B** and **C** on going from n = 1 to 7 (see below Figure 10). Thus, for the longest polyenes, the absorption spectra is dominated by transition **A** although, as we shall see later, the two-level model is insufficient to account for the quadratic hyperpolarizability of these compounds.

In polyenovanillins **14** and **15**, the asymmetry of the electronic density of the aromatic ring leads to a situation where the direction of μ, the ground state dipole moment, is not the same as that of $\Delta\mu$, the dipole moment difference between the first excited state and the ground state. The magnitude of angle α between μ and $\Delta\mu$ is a relevant parameter for the interpretation of EFISH measurements, because in the two-level model approximation the orientation of the vector part β_{vec} of the hyperpolarizability tensor is identical with that of $\Delta\mu$, and the EFISH method provides the projection β_μ of β_{vec} along the direction of μ. CNDO/S calculations predicted that the largest deviations between these two vectors should occur for the sulfur substituted derivatives **14** and **15**, and particularly for the latter (meta MeS) in conformation (**a**), where angle α was estimated to vary from ca. 70° (n = 1) to 30° (n = 7); in conformation (**b**) μ and $\Delta\mu$ were almost collinear in this case. In series **14** (para MeS) angles in the range 50−30° were calculated for both conformations, and smaller angles (40−20°) were predicted in series **13** (two MeO

(19) For series **13**, A = 97.392 nm, B = 165.51 nm, r^2 = 0.999; **14**, A = 81.764 nm, B = 211.69 nm, r^2 = 0.997; **15**, A = 89.907 nm, B = 184.17 nm, r^2 =0.998.

(20) (a) Blout, E. R.; Fields, M. *J. Am. Chem. Soc.* **1948**, *70*, 189−193. (b) Birge, R. R.; Pringle, W. C.; Leermakers, P. A. *J. Am. Chem. Soc.* **1971**, *93*, 6715−6726. (c) Das, P. K.; Becker, R. S. *J. Phys. Chem.* **1978**, *82*, 2081−2093. (d) *Ibid.* **1982**, *86*, 921−927. (e) Ros, M.; Groenen, E. J. J.; van Hermert, M. C. *J. Am. Chem. Soc.* **1992**, *114*, 6820−6827.

Table 3. Calculated Absorption Wavelengths and Oscillator Strengths for Polyenovanillins 13a, 15a ($n = 1$) and 13b, 15b ($n = 2$)[a]

	λ_{abs}^{fit}	λ_{abs}^{calc}	f	description[b]
13a		378	0.007	$0.82\chi_{35\rightarrow38} - 0.37\chi_{35\rightarrow40} + 0.27\chi_{35\rightarrow41} + 0.28\chi_{36\rightarrow48}$
	338	365/368	0.77/0.63	$0.98\chi_{37\rightarrow38}$
	305	308/316	0.15/0.04	$0.44\chi_{36\rightarrow38} + 0.86\chi_{37\rightarrow39}$
	300	279/278	0.39/0.92	$-0.82\chi_{36\rightarrow38} + 0.45\chi_{37\rightarrow39}$
13b	367	400/406	1.20/1.14	$0.98\chi_{42\rightarrow43}$
		385	0.01	$0.83\chi_{40\rightarrow43} - 0.24\chi_{40\rightarrow44} + 0.39\chi_{40\rightarrow45} + 0.25\chi_{40\rightarrow46}$
	343	317/323	0.15/0.03	$0.63\chi_{41\rightarrow43} + 0.70\chi_{42\rightarrow44}$
	303	298/298	0.26/0.89	$-0.72\chi_{41\rightarrow43} + 0.50\chi_{42\rightarrow44} + 0.42\chi_{42\rightarrow45}$
15a	349	387	0.36	$-0.97\chi_{37\rightarrow38}$
		376	0.3×10^{-2}	$0.86\chi_{35\rightarrow38} + 0.38\chi_{35\rightarrow40} + 0.28\chi_{35\rightarrow42}$
	310	330/331	0.24/0.07	$0.46\chi_{36\rightarrow38} + 0.86\chi_{37\rightarrow39}$
	305	310/300	0.74/1.23	$-0.87\chi_{36\rightarrow38} + 0.46\chi_{37\rightarrow39}$
15b	382	412/415	0.72/0.67	$0.96\chi_{42\rightarrow43}$
		383/384	$10^{-5}/10^{-3}$	$-0.83\chi_{40\rightarrow43} - 0.43\chi_{40\rightarrow45} + 0.26\chi_{40\rightarrow46}$
	367	349/346	0.58/0.37	$-0.93\chi_{41\rightarrow43} + 0.13\chi_{41\rightarrow45} + 0.30\chi_{42\rightarrow44}$
	332	327/325	0.35/0.95	$-0.29\chi_{41\rightarrow43} + 0.92\chi_{42\rightarrow44}$

[a] See structural formulas in Chart 1; λ_{abs}^{fit} (nm) were obtained from deconvolution of the experimental absorption spectra; λ_{abs}^{calc} (nm) and f are the corresponding CNDO/S calculated wavelengths and oscillator strengths of the transitions for conformations **a**/**b**. [b] For $n = 1$, HOMO = 37; for $n = 2$, HOMO = 42; $\chi_{i\rightarrow j}$ are the singly excited configuration functions.

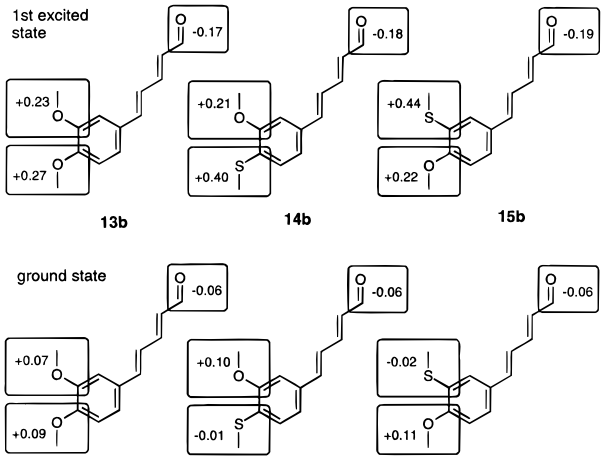


Figure 6. Calculated charge distribution in the ground state and first excited state of **13b**, **14b**, and **15b** ($n = 2$) in conformation **a**.

groups). The fact that the thiomethyl group is a weaker donor than the methoxy group in the ground state, while it exhibits a higher polarizability in the excited state (see Figure 6), is certainly at the origin of the large difference between the directions of μ and $\Delta\mu$ (and in turn of β_{vec}) in the sulfur-substituted derivatives **14** and **15**.

The order of magnitude of $\Delta\mu$ was assessed by solvatochromism experiments for series **13**. Although this method, based on the solvent-induced shifts of electronic absorption and fluorescence bands, is less accurate than electrical dichroism, electrical polarization of fluorescence, or Stark splitting of rotational spectra, it has often been used for the determination of the magnitude of the excited state dipole moment μ_e due to its easy implementation. Different expressions leading to the spectral shifts of the bands can be used;[21] these relationships are all based on the Onsager model,[22] which assumes that the solute molecule occupies a spherical cavity of radius a within the solvent considered as an homogeneous continuous medium of dielectric constant ϵ and refractive index n. In this work we used the equation of Lippert (eq V-2),[23] which relates

$$\nu_a - \nu_f = \frac{2}{hc}\left(\frac{\epsilon - 1}{2\epsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right)\frac{\Delta\mu^2}{a^3} + \text{C}te \quad \text{(V-2)}$$

the Stokes shift ($\nu_a - \nu_f$) of the fluorescence vs the absorption frequency to relevant characteristics of the molecule and of the medium. This equation is well suited for polyenovanillins since it does not involve, contrary to other relationships,[21] the collinearity of μ and $\Delta\mu$ but provides the absolute value of $\Delta\mu$.

Table 4. Solvatochromism of the Fluorescence Spectra for Polyenovanillins 13[a]

	13c	**13d**	**13e**	**13f′**
λ^f (nm) in Solvent				
cyclohexane	*b*	*b*	626	643
benzene	482	545	625	663
dioxane	491	552	591	662
chloroform	519	573	659	700
dichloromethane	533	610	678	718
acetone	535	610	678	725
acetonitrile	552	627	692	730
dimethyl sulfoxide	560	637	694	761
molecular volume V (Å^3)	238	266	294	373
cavity radius a (Å)	3.8	4.0	4.1	4.5
$\Delta\mu_{exp}$ (D)	7.0	7.4	7.5	7.7
$\Delta\mu_{calc}$ (D)	10.9	10.6	10.0	9.6

[a] V is the molecular volume calculated by using the volume increments of Bondi; a is the solvent cavity radius; $\Delta\mu_{exp}$ was derived from the solvatochromism data using eq V-2, and $\Delta\mu_{calc}$ was obtained from CNDO/S calculations. [b] The maximum of the fluorescence band was overlapped by Raman lines due to the solvent.

The fluorescence spectra of **13** with three to six double bonds consist of a strong single band, which shows a large bathochromic shift when the solvent refractive index n increases (Table 4), whereas only a small shift is observed in the absorption spectra. The fluorescence of the shortest derivatives ($n = 1$ and 2) was very weak, and these compounds were not included in the study. Measurements of the absorption and fluorescence maxima in several solvents of known dielectric constants and refractive indexes allowed the calculation of the slope $2\Delta\mu^2/hca^3$ of eq V-2; the cavity radius a was

(21) Bakhshiev, N. G.; Knyazhanskii, M. I.; Minkin, V. I.; Osipov, O. A.; Saidov, G. V. *Russ. Chem. Rev.* **1969**, *38*, 740−754 and references therein.

(22) Onsager, L. *J. Am. Chem. Soc.* **1936**, *58*, 1486−1493.

(23) Lippert, E. *Z. Electrochem.* **1957**, *61*, 962.

estimated from the molecular van der Waals volumes V of the solute, calculated by using the group increments of Bondi.[24] Values of $\Delta\mu$ obtained by this method and by CNDO/S calculations[25] are assembled in Table 4. The agreement between the two sets of data can be considered satisfactory, if we consider not only the values of $\Delta\mu$ but also their variations with the conjugation length, which will be considered in section VII.[26]

VI. EFISH Measurements

Second-order molecular polarizability analyses were performed using a Q-switched mode-locked Nd^{3+}:YAG laser emitting at 1.34 μm by the electric field induced second harmonic generation (EFISH) method.[27] The laser delivers pulse trains of total duration envelope around 90 ns, each pulse duration being 160 ps. The molecules to be measured were dissolved in chloroform used as a reference,[28] at various concentrations x (between 5×10^{-3} and 10^{-4} M^{-1}) and the solutions were placed in a wedge-shaped cell. A high-voltage pulse (around 5 kV), synchronized with the laser pulse, breaks the centrosymmetry of the liquid by dipolar orientation of the molecules. Translation of this cell perpendicular to the beam direction modulates the second harmonic signal into Maker fringes. The amplitude and the periodicity of the fringing pattern are related to the macroscopic susceptibility $\Gamma(x)$ of the solution and to its coherence length $l_c(x)$. Calibrations are made with respect to the pure solvent.[29] $\Gamma(x)$ is related to the microscopic hyperpolarizabilities of the solvent γ_s and of the dissolved molecule γ_m by eq VI-1, where ρ is the

$$\Gamma(x) = \frac{Nf\varrho}{1 + x}\left(\frac{\gamma_s}{M_s} + x\frac{\gamma_m}{M_m}\right) \qquad \text{(VI-1)}$$

density of the solvent, and N the Avogadro number; f is an average local field factor which is expressed as $f = f_0 f_\omega^2 f_{2\omega}$, where $f_{0,\omega,2\omega} = (\epsilon_\infty + 2)\epsilon_{0,\omega,2\omega}/(\epsilon_\infty + 2\epsilon_{0,\omega,2\omega})$, ϵ_∞ is the high-frequency contribution to the dielectric constant, and $\epsilon_{0,\omega,2\omega}$ the dielectric constant at frequencies 0, ω, 2ω, respectively. These local fields are infered from Onsager's theory;[30] in the limit where $\epsilon_\infty = n_\omega^2$ or $n_{2\omega}^2$, the factors $f_{\omega,2\omega}$ correspond to the Lorentz−Lorentz factor $f_{\omega,2\omega} = (n_{\omega,2\omega}^2 + 2)/3$; M_s and M_m are the molecular weights of the solvent and of the solute, and γ_m is given by eq VI-2, where $\beta_\mu = \beta_{yyy} + \beta_{yxx} + \beta_{yzz} \approx \beta_{yyy}$ for one-dimensional charge-transfer (CT) molecules with the CT axis parallel to y.

Table 5. Experimental (EFISH) and Calculated Quadratic Hyperpolarizabilities (in 10^{-30} esu) for Polyenovanillins 13−15

	n	$\beta_{exp}^{2\omega}$	β_{exp}^{0}	β_{vec}^{0}	β_{μ}^{0}	β_{av}^{0}
13a	1	12	8	18/17	15/15	15
13b	2	31	20	32/32	28/28	28
13c	3	62	38	53/51	47/45	46
13d	4	119	69	75/72	69/66	68
13e	5	190	102	96/93	89/86	88
13f	6	282	140	119/117	111/109	110
13g	7			139/139	131/130	130
14a	1	18	12	31/30	22/20	21
14b	2	31	20	53/52	42/37	40
14c	3	36	22	79/77	64/58	61
14d	4	151	84	104/98	87/78	83
14e	5	184	97	127/124	107/101	104
14f	6	345	170	155/149	134/125	129
14g	7			174/168	152/143	147
15a	1	6	4	18/17	10/17	13
15b	2	12	8	30/30	20/29	25
15c	3	66	40	45/44	33/40	37
15d	4	74	42	64/60	50/58	54
15e	5			92/87	76/84	80
15f	6	306	152	113/113	94/112	103
15g	7			133/134	112/130	121

$$\gamma_m = \gamma_e + \frac{\mu\beta_\mu}{5kT} \qquad \text{(VI-2)}$$

The cubic contribution γ_e to the total hyperpolarizabity γ_m can be neglected in small molecules (p-nitroaniline, etc.). However, it may become significant for larger conjugated molecules (up to 20% of γ_m), and this circumstance could lead to an overestimation of the experimental β values as compared to the calculated ones.[31] The sign of β is determined by studying the variations of $\Gamma(x)$ as a function of x; if β is negative, Γ first decreases with increasing x and cancels out when the contribution from the solvent is exactly compensated by that of the dissolved NLO molecule. Then the $\Gamma(x)$ value increases because it is dominated by the contribution of the solute. Further details on the EFISH experimental methodology are reported elsewhere.[32] The ground-state dipole moment was determined by the standard method of Guggenheim.[33]

VII. Discussion

For the three series **13**−**15**, the data assembled in Table 5 indicate that the magnitude of $\beta_{exp}^{2\omega}$ (EFISH, 1.34 μm) increases steadily from ca. 10 ($n = 1$) to ca. 345×10^{-30} esu ($n = 6$), the largest value being obtained for **14f′** (MeS in para). The same trend holds for the static hyperpolarizability β_{exp}^{0}, which was evaluated by means of the two-level model,[34] although, as discussed

(24) Bondi, A. *J. Phys. Chem.* **1968**, *68*, 441−451. Bondi, A. *Physical Properties of Molecular Crystals, Liquids, and Glasses*; Wiley: New York, 1968. Kitaigorodsky, A. I. *Molecular crystals and molecules*, Academic Press: London, 1973. Gavezzoti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220−5225.

(25) These $\Delta\mu$ were calculated according to: Lalama, S. J.; Garito, A. F. *Phys. Rev.* A **1979**, *20*, 1179−1194. In these calculations, configuration interaction is applied only to excited state.

(26) These solvatochromism measurements were carried out in order to verify the trend of the variation of $\Delta\mu$ vs m provided by the CNDO/S calculations. The use of an ellipsoidal model (ab^2) instead of the spherical Onsager model would perhaps provide better values of $\Delta\mu$, but the trend of their variations with m would not be affected.

(27) Oudar, J. L. *J. Chem. Phys.* **1977**, *67*, 446−457.

(28) Although dipole−dipole interactions between solvent and solute does exist, they have only a moderate influence on electronic properties of the molecules investigated here. For example, dipole moments values measured in dioxane (nonpolar) and in chloroform are very similar (the differences are within the experimental error); β values measured in acetone (with a higher dielectric constant) and in chloroform are also very close.

(29) For chloroform, $\Gamma = 7.7 \times 10^{-14}$ esu and $\gamma = 2.4 \times 10^{-36}$ esu for EFISH at 1.34 μm.

(30) See ref 22.

(31) A systematic investigation of second and third-order contributions to γ_{EFISH} in similar polyenes has been previously reported. For $n = 6$ double bonds, the electronic (third-order contribution) is 21% after frequency dispersion corrections: Messier, J.; Kajzar, F.; Sentein, C.; Barzoukas, M.; Zyss, J.; Blanchard-Desce, M.; Lehn, J. M. *Nonlinear Opt.* **1992**, *2*, 53−70.

(32) See ref 26 and: Ledoux, I.; Zyss J. *Chem. Phys.* **1982**, *73*, 203−213.

(33) Guggenheim E. A. *Trans. Faraday Soc.* **1949**, *G45*, 203.

(34) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664−2668.

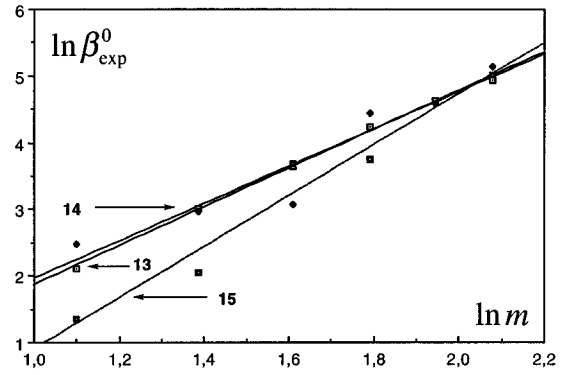


Figure 7. Plot of ln β^0_{exp} vs ln m in **13**−**15** ($m = n + 2$).

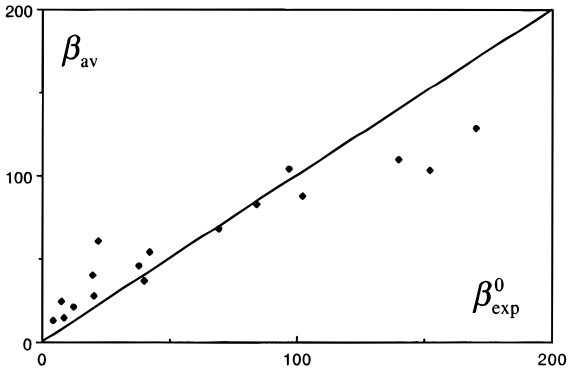


Figure 8. Plot of β_{av} vs β^0_{exp}.

below, the latter is probably inappropriate for the longest polyenes;[35] β^0_{exp} was obtained by dividing $\beta^{2\omega}_{exp}$ by the dispersion factor (eq VII-1) where W is the energy of the lowest excited state, estimated from the absorption spectra, and $\hbar\omega$ is the energy of the applied laser.

$$f(W,\omega) = 1/\{[1 - (2\hbar\omega/W)^2][1 - (\hbar\omega/W)^2]\} \quad \text{(VII-1)}$$

As in other push−pull polyenes,[36,37] the dependence of β^0_{exp} vs the conjugation length m ($m = n + 2$) in polyenovanillins does not show evidence of saturation when n increases[38] and is of the form $\beta^0_{exp} = km^{\alpha}$, with α = 2.9, 2.8, and 3.8 for series **13**, **14**, and **15**, respectively (Figure 7).[39] This behavior was satisfactorily reproduced by CNDO/S calculations. Assuming that the experimental hyperpolarizability reflects the contributions of conformations **a** and **b**, which are equally populated, the EFISH data β_{exp} have to be compared with β_{av}, the average of the calculated β_{μ} for each conformation. These data are assembled in Table 5, and a plot of β_{exp} vs β_{av} is shown in Figure 8; there is generally a good agreement between the experimental

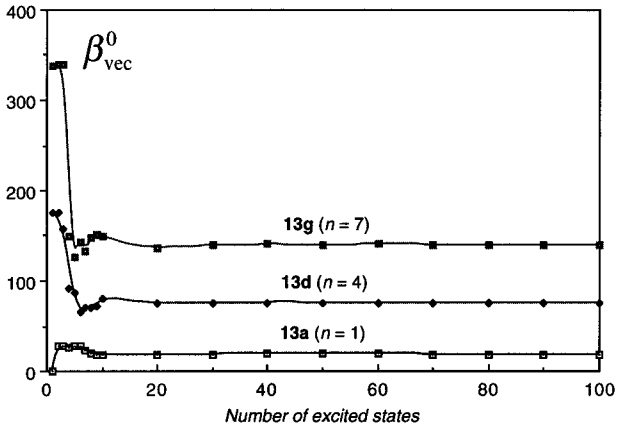


Figure 9. Plot of β^0_{vec} (series **13**) as a function of the number of excited states taken into account in the CNDO/S calculation.

and calculated data. However, although the calculated β_{av} correctly reproduced the trend of the experimental variation of β^0_{exp} with m, the exponents were predicted to be 2.0, 1.8, and 2.1, respectively, figures that are appreciably smaller than those derived from the two-level model. One of the reasons for this difference could originate from the fact that, when the length of the chain increases, excited states other than the lowest CT state convey a significant negative contribution, decreasing the hyperpolarizability (Figure 9). Otherwise stated, the two-level model, which ignores these additional states, leads to overestimate the magnitude of β^0_{exp} and this overestimation in turn leads to exponents that are too large. This trend seems to be general in all push−pull polyenes that we have investigated by quantum calculations (with *p*-methoxyphenyl, *p*-(dimethylamino)phenyl, vanillyl, thiovanillyl, phenyl, or hydrogen as the donor group and aldehyde as the acceptor); this behavior has already been pointed out in other systems[40] and, as in the case of long polyenovanillins, the calculated β values have been found to be one-half of the two-level value.

A systematic analysis of the different contributions to β values has been carried out. In fact, the decrease of β seems to arise principally from the contribution of a higher excited state (q), which corresponds mainly to the mixing of HOMO → LUMO+1 and HOMO−1→ LUMO transitions. A more accurate evaluation of the static hyperpolarizability would require utilization of eq VII-2[41] where x is the direction of charge transfer (all

$$\beta_{xxx} = -\frac{e^3}{8\hbar^2}\left[\left(12\frac{r^x_0 r^x_{1q} r^x_{01}}{\omega_1\omega_q}\right) + 12\left(\frac{(r^x_{01})^2\,\Delta\mu^x_1}{\omega_1^2}\right) + 12\left(\frac{(r^x_{0q})^2\,\Delta\mu_q{}^x}{\omega_q^2}\right)\right] \quad \text{(VII-2)}$$

vectors involved in eq VII-2 are parallel or antiparallel to x), r^x_{01}, r^x_{0q} are the matrix elements of the xth components of the dipole operator between the ground state and the excited states 1 and q, respectively,[42] and

(35) As will be shown below, the two-level model is inadequate to describe the dispersion of β. However, the knowledge of β^0_{exp} is necessary for the comparison with the calculated values, which points out the contribution of higher excited states for the long-chain polyenes.

(36) Blanchard-Desce, M.; Lehn, J.-M.; Barzoukas, M.; Ledoux, I.; Zyss, J. *Chem. Phys.* **1994**, *181*, 281−289.

(37) Meyers, F.; Bredas, J. L.; Zyss, J. *J. Am. Chem. Soc.* **1992**, *114*, 2914−2921 and references therein.

(38) This trend seems to be general in these systems; in push−pull polyenes containing benzodithia or *p*-$Me_2N(C_6H_4)$ groups the quadratic nonlinearity increases steeply up to n = 9; moreover, in symmetrical systems the saturation of the cubic hyperpolarizability γ is observed only beyond 120 double bonds.[1c,d]

(39) Exponents α are markedly smaller when the phenyl ring is not taken into account ($m = n$): 1.6, 1.5, and 2.1 for **13**, **14**, and **15**, respectively.

(40) Kanis, D. R., Marks, T. J., Ratner, M. A. *Nonlinear Opt.* **1994**, *6*, 317−335. Kanis, D. R.; Ratner, M. A., Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242.

(41) Ward, J. F. *Rev. Mod. Phys.* **1965**, *37*, 1−18. Ward, J. F.; New, G. H. C. *Phys. Rev.* **1969**, *185*, 57−72. Orr, B. J.; Ward, J. F. *Mol. Phys.* **1971**, *20*, 513−526.

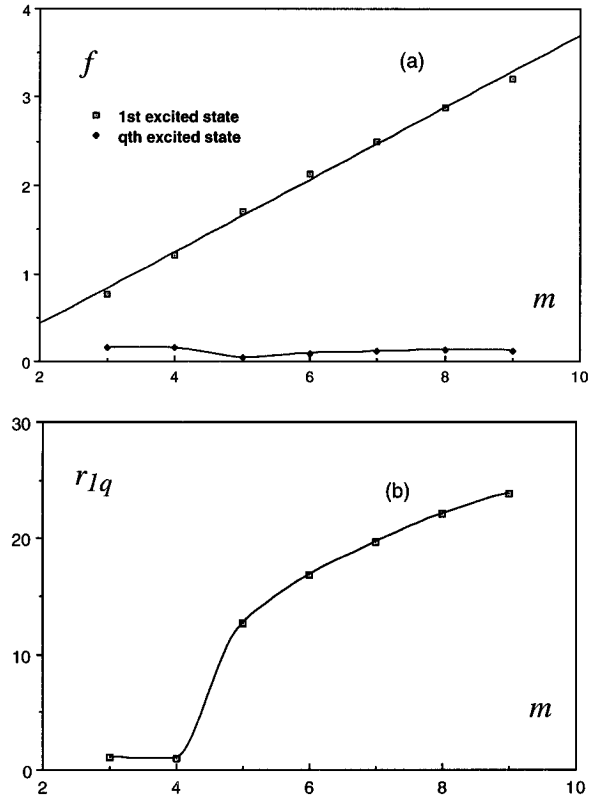


Figure 10. (a) Oscillator strengths of the most contributing transitions (1 and *q*) to β, (b) norme of the dipole operator $\vec{r}_{1q}$ between the excited states 1 and q as a function of the conjugation length in **13**.

r^x_{1q} corresponds to the dipole operator between the excited states 1 and *q*.

For instance, Figure 10 specifically shows the situation in series **13**. The negative contribution of the first term of eq VII-2 appears to be significant for $n \geq 3$ (Figure 9) as a consequence of the increase of $\vec{r}_{1q}$. The contribution of the third term is negligible because of the weak oscillator strength of the *q*th transition.[43] Further discussion of this point must await, however, that relevant experimental data be available on the excited-state properties of these compounds.

We now turn to a discussion of the relative efficiency of the donor groups in series **13**−**15**. Earlier studies have indicated that a *p*-MeS−Ar− group could be more effective than a *p*-MeO−Ar− group to enhance the quadratic hyperpolarizability in push−pull molecules.[1a,b,5] The EFISH measurements do not actually reflect the efficiency of this donor in the case of polyenovanillins, for which the magnitude of β^0_{exp} is approximately the same for the para-substituted RO and RS derivatives (**13** and **14**, respectively). This behavior could actually be correctly explained by quantum calculations.

The better efficiency of the thiovanillyl group, compared to the vanillyl group, can in fact be established when β_{vec}, instead of β_{av}, is considered; in effect the magnitude of β_{vec} and β_{av} are similar for series **13**, while β_{vec} is distinctly greater than β_{av} for **14** (see Table 5 and Figure 12). This feature is due to the fact that, as stated above, the angle between μ and β_{vec} is much larger in **14** than it is in **13** or **15** (see Figure 11, where the direction of $\Delta\mu$ is the same as that of β_{vec}).[44] These results emphasize the usefulness of information provided by quantum calculations in molecules for which μ and $\Delta\mu$ are not parallel, since EFISH measurements can only yield approximate values of β in this case.

As expected from these calculations, the isothiovanillin series **15** exhibits smaller values of β^0_{exp} than the vanillyl and thiovanillyl series **13** and **14**; this is particularly obvious for the shortest compounds, but the interesting point is that the difference tends to decrease as the chain length increases (see Figure 7).[45] The same trend has recently been observed between molecules containing benzodithia− and *p*-$Me_2N(C_6H_4)$− donor groups.[36] This trend, which seems to be general for push−pull polyenes, is also verified by quantum calculation. Figure 12 shows the variations of ln β_{vec} vs ln *m* for three series of polyenovanillins **13**−**15**. This behavior can be explained in the following way: in the two-level approximation (we assume here that the contribution of the lowest CT state remains dominant), the major component of the β tensor in a static field can be expressed as eq VII-3, where the oscillator strength *f* is defined as eq VII-4 and λ, the wavelength of the first CT transition, as $2\pi c/\omega$.

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

$$f = \frac{2m}{e^2\hbar}\omega\mu_{CT}{}^2 \qquad \text{(VII-4)}$$

The theoretical variations of *f* and $\Delta\mu$ with *m* are reported Figure 13. In the three series, the $\Delta\mu$'s do not show a great change with *m*, in agreement with the solvatochromism experiments reported in Table 4 for **13**; the observed decrease of the difference between the donor groups should therefore originate from the variations of *f* and λ (Figure 5) with *m*, which in fact follow the same trend as the variations of β itself. Figure 14 shows, for series **13**, with $m = 4$, 6, and 9, the way in which the HOMO and LUMO orbitals involved in the first excited state are modified when the number of double bonds increases. It becomes clear that for large values of *m* the HOMO → LUMO transition corresponds not to a charge transfer between the donor and the acceptor (this is consistent with the fact that the charge borne by the aldehyde group in the excited state is invariant with *m*) but rather to a charge transfer from the benzene ring toward the polyenic chain itself, with only a weak contribution of the donor and acceptor groups.[46] This leads to a situation where the excited state of the longest polyenes becomes almost independent of the nature of the donor, and where the aldehyde group is less acceptor in character when *m* is increased. The constancy of $\Delta\mu$ for $m > 5$ (i.e., $n > 3$) then arises from the localization of the charge on the chain.

(42) The square of these matrix elements is proportional to the oscillator strength of the transition.

(43) The oscillator strengths of the transitions 1 and *q* are proportional respectively to $r_{01}{}^2$ and $r_{0q}{}^2$.

(44) The angle between β_{vec} and $\Delta\mu$ never exceeds 10° in these compounds.

(45) The decrease of the difference between the logarithmic β values for the three donors is actually due to the decrease of the ratio of the corresponding β's.

(46) The contribution of the substituents is expressed by the different values of $\Delta\mu$ for the series **13**, **14**, and **15**.

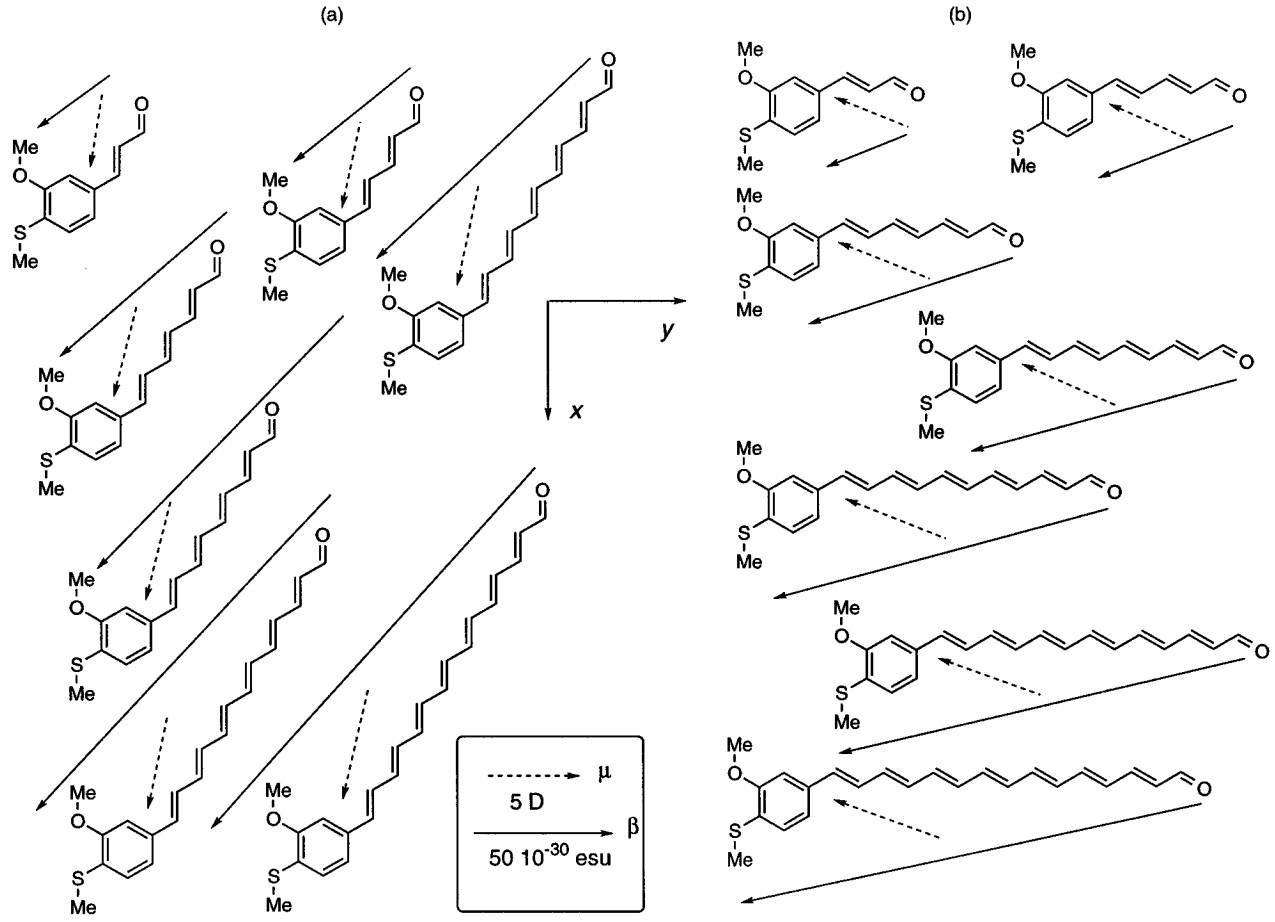


Figure 11. Angle between μ and β_{vec} (a) in conformations **a** and (b) in conformation **b** of **14**.

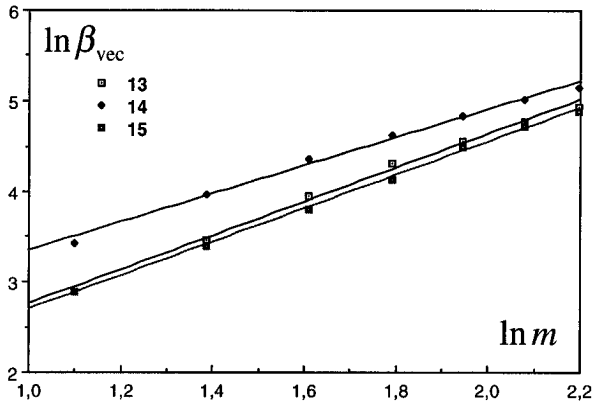


Figure 12. Plot of ln β_{vec} vs ln m for series **13**, **14**, and **15**.

VIII. Conclusion

Twenty-five [*n*]-polyenovanillins with $n = 1-6$ have been prepared via a Wittig−Horner polyvinylogation method providing these compounds in fair yield in a straightforward manner. Their structures, conformations, and spectroscopic properties have been investigated by NMR, X-ray, electronic absorption, and fluorescence spectroscopies and molecular modeling techniques. Their quadratic hyperpolarizabilities (β) have been measured (EFISH) and interpreted in light of semiempirical quantum calculations. The main conclusions of these investigations can be summarized as follows: (i) experimentally, there is no saturation of the hyperpolarizability enhancement when the conjugation length increases at least up to six double bonds (the largest polyenes studied in this work); (ii) the theoretical

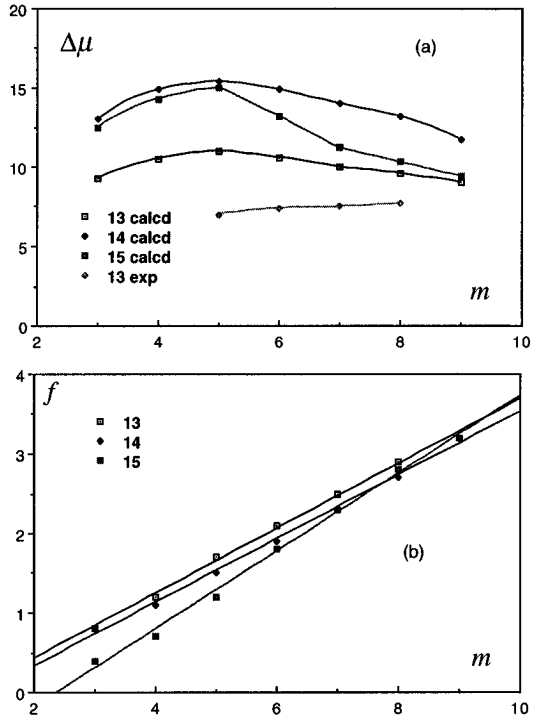


Figure 13. (a) Theoretical (**13**, **14**, and **15**) and experimental (**13**) variations of $\Delta\mu$ with m; (b) theoretical variation of the oscillator strength f of the first excited state in **13**−**15**.

calculations of β reveals that, particularly in the sulfur substituted compounds, there is a significant deviation of the direction of the excited-state dipole moment with respect to the ground state one, and for this reason the

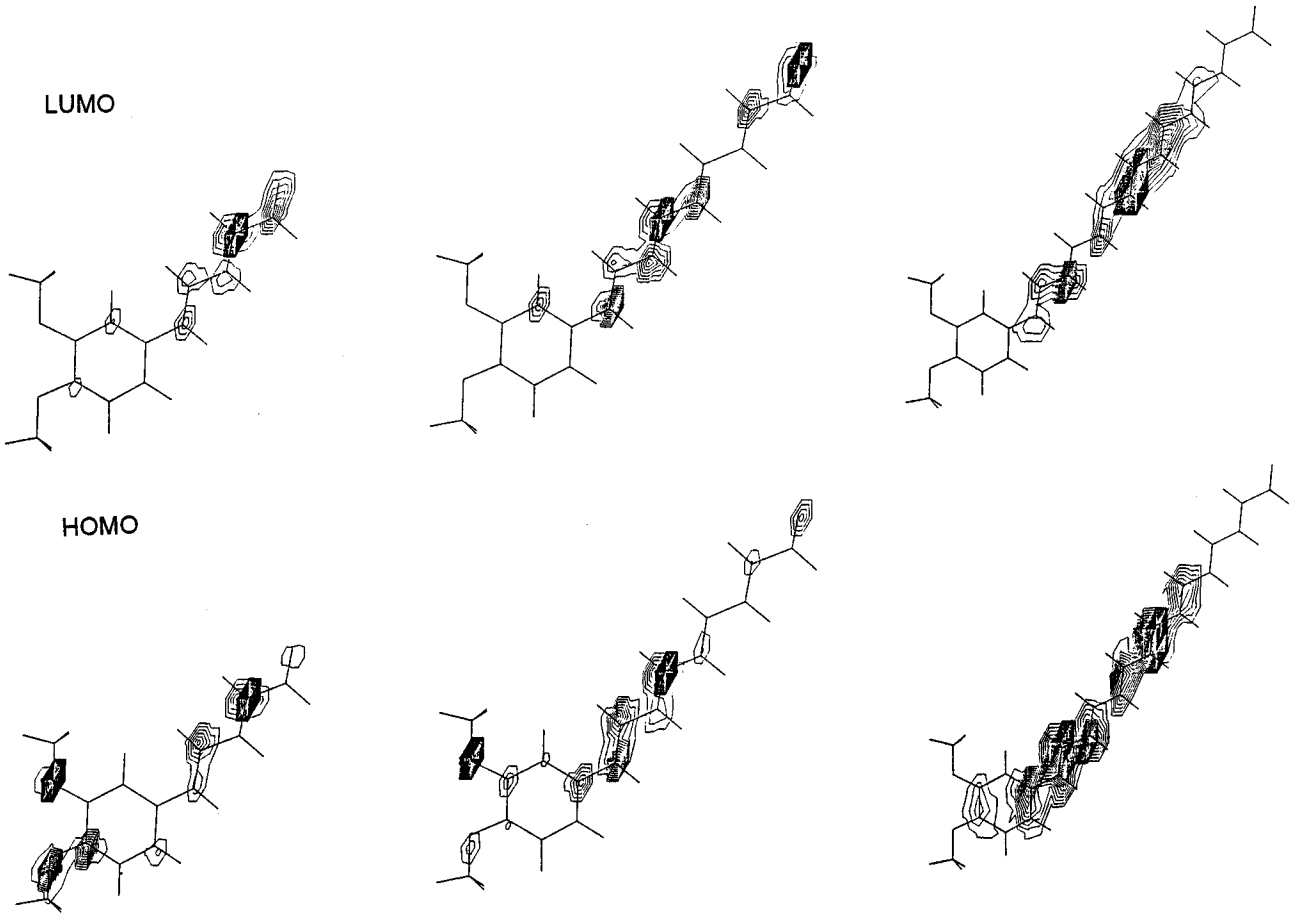


Figure 14. AM1 calculated contours of Ψ^2 for the HOMO and LUMO orbitals in **13b**, **13d**, and **13g**.

EFISH method can provide only underestimated values of β; (iii) the calculations point out that the two-level model is no longer valid beyond three or four double bonds, where the negative contribution of additional excited states become significant; (iv) it is also found that when the conjugation length increases, the charge transfer between the donor and acceptor ends of the molecule turns into transfer from the benzene ring to the polyene chain. Finally, if the quadratic hyperpolarizabilities of these polyenovanillins are of the same order of magnitude as those of other push−pull polyenes of the same length, they offer several advantages which should make these compounds good candidates for NLO materials: they are accessible in fair yield via a straightforward synthesis (the longest polyenovanillines are accessible in only two steps from vanillin derivatives), they show a remarkable thermal stability (decomposition temperature at 195−200 °C), and suitably functionalized derivatives form thin layers of good quality.[47]

Experimental Section

General Methods. Reactions involving polyenes were carried out under argon, with protection against direct daylight. Chromatographic separations were done on Merck silica gel 60 (0.040−0.063 mm). For all spectroscopic studies, the polyene solutions were handled in the dark to prevent isomerization. NMR spectra were taken on a Varian Unity$^+$ 500 operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Melting points were recorded in sealed aluminum pans on a Perkin-Elmer DSC7 microcalorimeter, with a simultaneous check of purity and of decomposition temperatures. UV−vis absorption spectra were recorded on a Cary 219 instrument, Fluorescence spectra were measured on a SPEX 1681 spectrofluorimeter, IR spectra (in KBr) were recorded on a Perkin-Elmer FTIR 1600 spectrometer. Molecular modeling calculations were carried out with SYBYL (including MOPAC), PCMODEL, and HYPERCHEM software. All calculations were run on IBM RS6000 or Silicon Graphics RS4400 workstations.

Crystal Structure Determination. [3]-Polyenovanillin **15c** [$C_{15}H_{16}0_2S$, MW 260.35] was crystallized from diethyl ether and gave suitable plates for data collection at 22 °C on a Nonius CAD4 diffractometer using graphite monochromatized Cu Kα radiation (1.540 56 Å). A crystal of 0.04 × 0.12 × 0.30 mm was used. Lattice parameters were refined by a least-squares fit of 25 $(\theta,\varphi,\omega,\kappa)_{hkl}$ reflections. The crystal was monoclinic, $P2_1$, a 17.486(2), b 7.923(4), c 4.973(2) Å, β 90.07 (4)°, $Z = 2$, $d_{calc} = 1.255$ g cm^{-3}. Three standard reflections were measured every hour to test intensity variations, and a test was performed to check the orientation of the crystal every 100 measurements. A total of 3304 reflections were collected (scan mode $\Omega-2\theta$, θ range 1−73°, collection range $+h$, $+k$, $+l$, abs coeff (μ) 19.7 cm^{-1}), of which 2689 had $I > 3\sigma(I)$, and 2182 were used in refinement. The structure was solved by MULTAN[48] and refined by SHELX.[49] Hydrogen atoms were placed in their calculated positions with the geometrical constraint C−H = 1.08 Å and refined riding on C; 168 parameters were refined to a final R_W of 0.083. Relevant torsion angles and bond lengths are assembled in Table 1. Positional parameters are indicated in Table 6.

(47) Brotin, T.; Chauvet, J.-P.; Andraud, C., Collet, A., to be published.

(48) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. *MULTAN 80*, A System of Computer Program for the Automatic Solution of Crystal Structures from X-ray Diffraction Data, University Of York, England, and Louvain, Belgium, 1980.

(49) Sheldrick, G. M. SHELX 76, Computer Program for Crystal Structure Determination, University of Cambridge, England, 1976.

Table 6. Positional Parameters and Their Estimated Standard Deviations for 15c[a,b]

atom	x	y	z	B (Å^2)
S	0.4221(1)	0.2168	−0.0162(4)	4.77(4)
C(g)	0.3970(5)	0.391(1)	0.197(2)	5.6(2)
C(e)	0.3466(4)	0.0749(9)	0.034(1)	3.7(1)
C(a)	0.2883(4)	0.0949(9)	0.221(1)	3.8(1)
C(f)	0.2306(3)	−0.0215(9)	0.254(1)	3.6(1)
C(b)	0.2326(4)	−0.168(1)	0.089(2)	4.9(2)
C(c)	0.2902(4)	−0.189(1)	−0.092(1)	4.4(2)
C(d)	0.3469(3)	−0.073(1)	−0.120(1)	3.9(1)
O	0.4086(3)	−0.0858(8)	−0.290(1)	5.5(1)
C(g)	0.4126(5)	−0.235(1)	−0.456(2)	5.7(2)
C(7)	0.1716(4)	0.0081(9)	0.454(2)	4.2(2)
C(6)	0.1045(3)	−0.0707(9)	0.487(1)	3.8(1)
C(5)	0.0531(4)	−0.0286(9)	0.705(1)	4.0(1)
C(4)	−0.0157(4)	−0.095(1)	0.753(1)	4.0(1)
C(3)	−0.0612(4)	−0.0398(9)	0.980(1)	3.9(1)
C(2)	−0.1319(4)	−0.096(1)	1.043(1)	4.3(2)
C(1)	−0.1706(4)	−0.031(1)	1.282(2)	5.2(2)
O=	−0.2311(3)	−0.0759(9)	1.362(1)	7.3(2)
H(a)	0.2885(4)	0.2060(9)	0.346(1)	
H(b)	0.1880(4)	−0.262(1)	0.104(2)	
H(c)	0.2913(4)	−0.301(1)	−0.215(1)	
H(g0)	0.4597(5)	−0.216(1)	−0.594(2)	
H(g1)	0.3617(5)	−0.267(1)	−0.568(2)	
H(g2)	0.4263(5)	−0.336(1)	−0.319(2)	
H(7)	0.1826(4)	0.1109(9)	0.591(2)	
H(6)	0.0884(3)	−0.1698(9)	0.349(1)	
H(5)	0.0725(4)	0.0671(9)	0.844(1)	
H(4)	−0.0374(4)	−0.192(1)	0.622(1)	
H(3)	−0.0368(4)	0.0554(9)	1.110(1)	
H(2)	−0.1599(4)	−0.188(1)	0.916(1)	
H(1)	−0.1416(4)	0.065(1)	1.397(2)	
H(h0)	0.4408(5)	0.485(1)	0.167(2)	
H(h1)	0.3993(5)	0.346(1)	0.402(2)	
H(h2)	0.3415(5)	0.446(1)	0.158(2)	

[a] Atom numbering in Figure 3. [b] $a = 17.486(2)$, $b = 7.923(4)$, $c = 4.973(2)$, $\beta = 90.07(4)°$.

Theoretical Calculations. The program used for CNDO/S calculations was derived from the QCPE 382 version,[50] in which the energy of the electronic excited states are refined by configuration interaction between singly excited states. The details of the method have been provided in ref 5, in which the set of parameters used in this work is referenced as *parametrization B*; in this parametrization, an internal dielectric constant is introduced by computing the monocentric bielectronic Coulomb integrals Γ_{AA} according to François et al.,[50] while for the other parameters the standard CNDO/S values have been used.[51]

3-(Methylthio)-4-hydroxybenzaldehyde (8). A 1 M solution of boron tribromide in dichloromethane (10.52 g, 0.042 mol) was added dropwise at −78 °C, under argon, to a stirred solution of 3-(methylthio)-4-methoxybenzaldehyde (**6**, 2.55 g, 14 mmol) in dichloromethane (90 mL, freshly distilled over $CaCl_2$). The mixture was allowed to warm to room temperature and stirred overnight. Water was added and the organic material was extracted with diethyl ether. The organic phase was then extracted with aqueous 2 M sodium hydroxide, and the alkaline extract was acidified with concentrated HCl and extracted with diethyl ether. The ether layer was dried over Na_2SO_4 and the solvent was stripped off to give a white solid which was eventually filtrated over silica gel (diethyl ether/pentane 1:1, R_f 0.37) to give the desired **8** (1.29 g, 55%), mp 99−100 °C (by dsc). Anal. Calcd for $C_8H_8O_2S$: C, 57.12; H, 4.79; O, 19.02. Found: C, 57.0; H, 4.8; O, 18.8. ^{1}H NMR ($CDCl_3$) δ 9.84 (1 H, s, CHO); 8.03 (1 H, d, H(a), $J_{a,b} = 2.0$ Hz); 7.77 (1 H, dd, H(b), $J_{b,c} = 8.5$ Hz, $J_{a,b} = 2.0$ Hz); 7.12 (1 H, s, OH); 7.09 (1 H, d, H(c), $J_{b,c} = 8.5$ Hz); 2.37 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 190.2, 161.3, 136.4, 132.6, 130.3, 122.7, 115.4, 19.5.

3-Hydroxy-4-(methylthio)benzaldehyde (7). To a stirred solution of 3-methoxy-4-(methylthio)benzaldehyde (**5**, 2 g, 11.9 mmol) in 185 mL of dichloromethane (freshly distilled over $CaCl_2$) at −78 °C under argon, was slowly added 35 mL of a 1 M solution of boron tribromide in dichloromethane. The orange solution was then stirred for 90 min at room temperature; water was added, and the organic material was extracted with diethyl ether. The organic extract was treated with aqueous 2 M NaOH and the water layer was acidified with concentrated HCl and extracted with diethyl ether to give a white solid which was filtrated over a short silica gel column (diethyl ether/pentane 1:1, R_f 0.43) to give the desired **7** (1.3 g, 65%), mp 116 °C (by dsc). Anal. Calcd for $C_8H_8O_2S$: C, 57.12; H, 4.79; O, 19.02. Found: C, 57.3; H, 4.8; O, 19.4. ^{1}H NMR ($CDCl_3$) δ 9.92 (1 H, s, CHO); 7.54 and 7.40 (3 H, m, arom H's); 6.35 (1 H, s, OH); 2.43 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 191.6, 155.3, 136.8, 131.7, 130.8, 122.6, 114.7, 17.9.

3-Butoxy-4-(methylthio)benzaldehyde (9). A solution of 1-bromobutane (0.82 g, 6 mmol) in 4 mL of anhydrous DMF was added to a stirred mixture of 3-hydroxy-4-(methylthio)-benzaldehyde (**7**, 0.83 g, 4.9 mmol) and dry K_2CO_3 (3.4 g, 25 mmol) in 50 mL of DMF at 80 °C. The mixture was stirred overnight under argon, then the organic material was extracted with diethyl ether, and the organic extract was washed with aqueous 1 M NaOH, then water, and brine. The crude product was column chromatographed (diethyl ether/pentane 30:70 then 50:50) to give 0.99 g (90%) of the desired **9** (yellow oil). Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; O, 14.27. Found: C, 64.4; H, 7.2; O, 14.5. ^{1}H NMR ($CDCl_3$) δ 9.87 (1 H, s, CHO); 7.40 (1 H, dd, H(b), $J_{a,b} = 1.5$ Hz, $J_{b,c} = 7.9$ Hz); 7.27 (1 H, d, H(a), $J_{a,b} = 1.5$ Hz); 7.17 (1 H, d, H(c), $J_{b,c} = 7.9$ Hz); 4.09 (2 H, t, OCH_2, $J = 6.6$ Hz); 2.45 (3 H, s, SCH_3); 1.84 (2 H, m, CH_2); 1.54 (2 H, m, CH_2); 0.97 (3 H, t, CH_3, $J = 7.3$ Hz). ^{13}C NMR ($CDCl_3$) δ 191.1, 155.1, 137.6, 133.5, 124.7, 123.4, 107.8, 66.4, 30.9, 19.1, 13.6.

4-Butoxy-3-(methylthio)benzaldehyde (10). This compound was prepared from 4-hydroxy-3-(methylthio)benzaldehyde (**8**, 1.35 g, 8 mmol), 1-bromobutane (1.4 g, 10.2 mmol), and K_2CO_3 (4.5 g, 32.8 mmol) as described above; yield 1.6 g (89%), oil. Anal. Calcd for $C_{12}H_{16}O_2S$: C, 64.25; H, 7.19; O, 14.27. Found: C, 64.1; H, 7.2; O, 14.5. ^{1}H NMR ($CDCl_3$) δ 9.83 (1 H, s, CHO); 7.62 (1 H, s, H(a); 7.59 (1 H, dd, H(b), $J_{a,b} = 2$ Hz, $J_{b,c} = 8.2$ Hz); 6.88 (1 H, d, H(c), $J_{b,c} = 8.2$ Hz); 4.11 (2 H, t, OCH_2, $J = 6.4$ Hz); 2.46 (3 H, s, SCH_3); 1.86 (2 H, m, CH_2); 1.55 (2 H, m, CH_2); 0.98 (3 H, t, CH_3, $J = 7.3$ Hz).

(*E*)-3-(3-Methoxy-4-(methylthio)phenyl)propenal (14a). *General Procedure A.* A solution of commercial (*Z*)-1-bromo-2-ethoxyethylene **I** (0.54 g, 3.6 mmol) in 20 mL of dry THF was cooled to −78 °C under argon, then 4 mL of *tert*-butyllithium (1.7 M in pentane) was added dropwise, and the mixture was stirred for 40 min. This was followed by addition of 3-methoxy-4-(methylthio)benzaldehyde (**5**, 0.6 g, 3.3 mmol) in ca. 5 mL of THF; the resulting yellow solution was stirred for 45 min at −78 °C and then was allowed to warm to room temperature. Hydrolysis was effected by adding 5 mL of 1 M HCl at ca. −50 °C followed by 1 h of stirring at room temperature. The organic material was extracted with diethyl ether, and the ether layer was washed with water and brine, dried over Na_2SO_4, and evaporated to dryness. Flash chromatography on silica gel (diethyl ether/pentane 50:50) afforded 0.54 g (79%) of pure **14a**, as pale yellow crystals (from a dichloromethane: pentane mixture), mp 92 °C (by dsc). Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; O, 15.36. Found: C, 63.6; H, 5.9; O, 15.1. ^{1}H NMR ($CDCl_3$) δ 9.67 (1 H, d, H(1), $J_{1,2} = 7.6$ Hz); 7.41 (1 H, d, H(3), $J_{2,3} = 16.0$ Hz); 7.14 (2 H, m, H(b) and H(c)); 6.97 (1 H, s, H(a)); 6.66 (1 H, dd, H(2), $J_{1,2} = 7.6$ Hz, $J_{2,3} = 16.0$ Hz); 3.92 (3 H, s, OCH_3); 2.45 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.4, 155.9, 152.4, 132.8, 131.2, 127.5, 124.7, 122.4, 108.2, 55.8, 14.1.

(*E*)-3-(4-Methoxy-3-(methylthio)phenyl)propenal (15a). This compound was prepared according to general procedure A, from 4-methoxy-3-(methylthio)benzaldehyde (**6**, 0.6 g, 3.3 mmol); yield 0.43 g (63%) of **15a**, pale yellow crystals (from dichloromethane/pentane), mp 96 °C (by dsc). Anal. Calcd for $C_{11}H_{12}O_2S$: C, 63.43; H, 5.81; O, 15.36. Found: C, 63.7; H, 5.7; O, 15.2. ^{1}H NMR ($CDCl_3$) δ 9.65 (1 H, d, H(1), $J_{1,2} =$

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(51) Del Bene, J.; Jaffé, H. H. *J. Chem. Phys.* **1968**, *48*, 1807.

7.6 Hz); 7.41 (1 H, d, H(3), $J_{2,3}$ = 15.9 Hz); 7.345 (1 H, dd, H(b), $J_{b,c}$ = 8.1 Hz, $J_{a,b}$ = 2.0 Hz); 7.32 (1 H, d, H(a), $J_{a,b}$ = 2.0 Hz); 6.85 (1 H, d, H(c), $J_{b,c}$ = 8.1 Hz); 6.61 (1 H, dd, H(2), $J_{2,3}$ = 15.9 Hz, $J_{1,2}$ = 7.6 Hz); 3.94 (3 H, s, OCH_3); 2.45 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.4, 158.5, 152.3, 128.5, 127.2, 127.1, 126.7, 125.3, 110.0, 56.0, 14.4.

(*E*)-3-(3,4-Dimethoxyphenyl)propenal (13a). This compound was prepared from veratraldehyde (0.5 g, 3 mmol) according to general procedure A, followed by flash chromatography (diethyl ether/pentane 60:40); the resulting **13a** (white solid, 0.46 g, 80%) was recrystallized from dichloromethane/pentane; mp 84 °C (by dsc). Anal. Calcd for $C_{11}H_{12}O_3$: C, 68.74; H, 6.29. Found: C, 68.7; H, 6.25. ^1H NMR ($CDCl_3$) δ 9.63 (1 H, d, H(1), $J_{1,2}$ = 7.7 Hz); 7.39 (1 H, d, H(3), $J_{2,3}$ = 15.8 Hz); 7.14 (1 H, dd, H(b), $J_{b,c}$ = 8.7 Hz, $J_{a,b}$ = 1.8 Hz); 7.05 (1 H, d, H(a), $J_{a,b}$ = 1.8 Hz); 6.88 (1 H, d, H(c), $J_{b,c}$ = 8.7 Hz); 6.58 (1 H, dd, H(2), $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 15.8 Hz); 3.91 (3 H, s, OCH_3); 3.90 (3 H, s, OCH_3). ^{13}C NMR ($CDCl_3$) δ 193.4, 152.7, 151.9, 149.3, 127.0, 126.6, 123.3, 111.1, 109.8, 56.0, 55.9.

(*E,E*)-5-(3-Methoxy-4-(methylthio)phenyl)penta-2,4-dienal (14b). *General Procedure B.* Potassium *tert*-butoxide (0.5 g, 1.05 equiv) was added under argon to a stirred solution of phosphonate **II** (1.2 g, 1 equiv) in anhydrous THF at −78 °C. After 90 min, 3-methoxy-4-(methylthio)benzaldehyde (**5**, 0.72 g, 0.8 equiv) in 3 mL of THF was added; after a further 15 min of stirring at −78 °C, the reaction mixture was allowed to warm to 0 °C and was stirred for 2 h at this temperature. Hydrolysis was effected by adding dropwise aqueous 2.5 M HCl at −50 °C followed by 1 h of stirring at room temperature. Extraction with diethyl ether (or dichloromethane) followed by flash chromatography on silica gel (diethyl ether/pentane 50:50) afforded a mixture of stereoisomers which was converted to the pure all-trans isomer by reaction with a catalytic amount of iodine in dichloromethane for 5 h at room temperature. The dichloromethane solution was washed with aqueous sodium thiosulfate then with brine, dried over sodium sulfate, and evaporated to dryness, to give the pure all-trans isomer **14b**, 0.61 g (66%), R_f 0.5 (diethyl ether/pentane 50:50); after another flash chromatography on silica gel (diethyl ether/pentane 50:50), the product was recrystallized from dichoromethane and pentane to give yellow orange crystals, mp 81 °C (by dsc). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; O, 13.66. Found: C, 66.7; H, 6.2; O, 13.7. ^1H NMR ($CDCl_3$) δ 9.59 (1 H, d, H(1), $J_{1,2}$ = 7.7 Hz); 7.22 (1 H, dd, H(3), $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 10.0 Hz); 7.10 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 7.07 (1 H, dd, H(b), $J_{a,b}$ = 1.5 Hz, $J_{b,c}$ = 8.0 Hz); 6.94 (1 H, d, H(a), $J_{a,b}$ = 1.5 Hz); 6.97−6.89 (2 H, m, H(4) and H(5)); 6.24 (1 H, dd, H(2), $J_{1,2}$ = 7.7 Hz, $J_{2,3}$ = 15.5 Hz); 3.92 (3 H, s, OCH_3); 2.43 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.2, 156.35, 151.7, 142.1, 133.3, 131.3, 130.5, 125.5, 125.4, 121.3, 108.0, 55.9, 14.4.

(*E,E*)-5-(4-Methoxy-3-(methylthio)phenyl)penta-2,4-dienal (15b). This compound was prepared according to general procedure B, using 4-methoxy-3-(methylthio)benzaldehyde (**6**, 0.65 g, 3.6 mmol) as the starting material. The crude product was flash chromatographed on silica gel (diethyl ether/pentane 50:50, R_f 0.5) to give a mixture of two stereoisomers which was converted to the all-trans isomer **15b** in the presence of iodine in dichloromethane to give yellow needles (0.63 g, 75%) after evaporating the solvent; this product was rechromatographed on silica gel (diethyl ether/pentane 50:50) and then recrystallized in a mixture of dichloromethane and pentane, mp 120 °C (by dsc). Anal. Calcd for $C_{13}H_{14}O_2S$: C, 66.64; H, 6.02; O, 13.66. Found: C, 66.4; H, 5.9; O, 13.6. ^1H NMR ($CDCl_3$) δ 9.59 (1 H, d, H(1), $J_{1,2}$ = 8.5 Hz); 7.285 (1 H, d, H(a), $J_{a,b}$ = 2.0 Hz); 7.27 (1 H, dd, H(b), $J_{a,b}$ = 2.0 Hz, $J_{b,c}$ = 8.0 Hz); 7.215 (1 H, dd, H(3), $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 10.5 Hz); 6.95−6.82 (2 H, m, H(4) and H(5)); 6.81 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 6.22 (1 H, dd, H(2), $J_{1,2}$ = 8.5 Hz, $J_{2,3}$ = 15.5 Hz); 3.91 (3 H, s, OCH_3); 2.45 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.25, 157.8, 152.0, 141.8, 130.9, 129.1, 128.2, 126.1, 125.4, 124.5, 110.3, 56.0, 14.9.

(*E,E*)-5-(3,4-Dimethoxyphenyl)penta-2,4-dienal (13b). This compound was prepared from veratraldehyde (0.95 g, 5.7 mmol) and phosphonate **II** according to general procedure B. The crude product was flash chromatographed on silica gel (diethyl ether/pentane 50:50, then 70:30) to give a mixture of stereoisomers which was converted to the all-trans isomer **13b** in the presence of iodine in dichloromethane; yellow crystals (0.83 g, 67%) after evaporating the solvent; this product was rechromatographed on silica gel (diethyl ether/pentane 70:30) and then recrystallized in a mixture of dichloromethane and pentane, mp 99 °C (by dsc). Anal. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47. Found: C, 71.4; H, 6.6. ^1H NMR ($CDCl_3$) δ 9.59 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.22 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 10.5 Hz); 7.05 (1 H, d, H(b), $J_{b,c}$ = 8.0 Hz); 7.01 (1 H, d, H(a), $J_{a,b}$ = 1.5 Hz); 6.94 (1 H, d, H(5), $J_{4,5}$ = 15.5 Hz); 6.85 (1 H, dd, H(4), $J_{4,5}$ = 15.5 Hz, $J_{3,4}$ = 10.5 Hz); 6.85 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 6.22 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 3.91 (3 H, s, OCH_3); 3.89 (3 H, s, OCH_3). ^{13}C NMR ($CDCl_3$) δ 193.25, 152.1, 150.9, 149.5, 142.3, 130.8, 128.9, 124.4, 121.9, 111.5, 109.7, 56.0 (2 C).

(*E,E*)-5-(3-Butoxy-4-(methylthio)phenyl)penta-2,4-dienal (14b′). This compound was prepared according to general procedure B, from 3-butoxy-4-(methylthio)benzaldehyde (**9**, 0.71 g, 3.2 mmol) and phosphonate **II**. The crude product was flash chromatographed on silica gel (diethyl ether/pentane 40:60) to give a mixture of two stereoisomers which was converted to the all-trans isomer **14b′** in the presence of iodine in dichloromethane; yellow crystals (0.72 g, 81%), after evaporating the solvent; these crystals are then rechromatographed on silica gel (diethyl ether/pentane 40:60) and then recrystallized in CH_2Cl_2/pentane, mp 75−76 °C (by dsc). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.53; H, 7.29; O, 11.58. Found: C, 69.6; H, 7.2; O, 11.4. ^1H NMR ($CDCl_3$) δ 9.59 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.24 (1 H, m, H(3)); 7.08 and 7.05 (2 H, m, H(c) and H(b)); 6.94 (1 H, s, H(a)); 6.97 and 6.90 (2 H, m, H(4) and H(5)); 6.24 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.06 (2 H, t, OCH_2, J = 6.5 Hz); 2.43 (3 H, s, SCH_3); 1.83 (2 H, m, CH_2); 1.54 (2 H, m, CH_2); 0.98 (3 H, t, CH_3, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 193.5, 155.6, 152.2, 142.4, 132.9, 131.1, 130.9, 125.2, 124.8, 121.2, 108.7, 68.5, 31.2, 19.3, 14.2, 13.9.

(*E,E*)-5-(3-Butoxy-4-methoxyphenyl)penta-2,4-dienal (13b′). This compound was prepared according to general procedure B, from 3-butoxy-4-methoxybenzaldehyde (**11**, 1 g, 4.8 mmol) and phosphonate **II**. The crude product was flash chromatographed on silica gel (diethyl ether/pentane 40:60) to give a mixture of two stereoisomers which was converted to the all-trans isomer **13b′** in the presence of iodine in dichloromethane; yellow crystals (0.8 g, 64%) after evaporating the solvent; the same procedure of purification described for compound **14b′** was applied, mp 55 °C (by dsc). Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.9; H, 7.9. ^1H NMR ($CDCl_3$) δ 9.58 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.22 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 10.5 Hz); 7.05 (1H, d, H(c), $J_{b,c}$ = 8.5 Hz); 7.01 (1 H, d, H(a), $J_{a,b}$ = 1.5 Hz); 6.93 (1 H, d, H(5), $J_{4,5}$ = 15.5 Hz); 6.86 (1 H, d, H(b), $J_{b,c}$ = 8.5 Hz); 6.85 (1 H, dd, H(4), $J_{4,5}$ = 15.5 Hz, $J_{3,4}$ = 10.5 Hz); 6.22 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.04 (2 H, t, OCH_2, J = 6.5 Hz); 3.88 (3 H, s, OCH_3); 1.84 (2 H, m, CH_2); 1.50 (2 H, m, CH_2); 0.98 (3 H, t, CH_3, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 193.5, 152.5, 151.2, 148.9, 142.6, 130.6, 128.6, 124.1, 121.85, 111.5, 110.9, 68.8, 56.0, 31.2, 19.2, 13.85.

(*E,E,E*)-7-(4-Methoxy-3-(methylthio)phenyl)hepta-2,4,6-trienal (15c). Compound **15c** was prepared from aldehyde **6** (0.8 g, 4.4 mmol) and phosphonate **III** (1.5 g, 5.4 mmol) according to general procedure B. The crude product was then purified by flash chromatography on silica gel (diethyl ether); orange crystals (0.79 g, 69%), mp 131−132 °C (by dsc) and then recrystallized from dichloromethane/pentane. Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19; O, 12.39. Found: C, 69.3; H, 6.4; O, 12.3. ^1H NMR ($CDCl_3$) δ 9.57 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.25 (1 H, d, H(a), $J_{a,b}$ = 1.5 Hz); 7.22 (1 H, dd, H(b), $J_{a,b}$ = 1.5 Hz, $J_{b,c}$ = 8.5 Hz); 7.15 (1 H, dd, H(3), $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 11.5 Hz); 6.83−6.70 (3 H, m, H(5), H(6) and H(7)); 6.80 (1 H, d, H(c), $J_{b,c}$ = 8.5 Hz); 6.51 (1 H, m, H(4)); 6.16 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.5 Hz); 3.90 (3 H, s, OCH_3); 2.45 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.5, 156.9, 151.9, 143.0, 137.8, 130.8, 129.7. 129.3, 127.7, 126.0, 125.3, 124.5, 110.1, 56.0, 14.7.

(*E,E,E*)-7-(3-Methoxy-4-(methylthio)phenyl)hepta-2,4,6-trienal (14c). The trienal **14c** was prepared from aldehyde **7** (1 g, 5.5 mmol) and phosphonate **III** (1.82 g, 6.6 mmol)

according to general procedure B. After purification by flash chromatography (diethyl ether and pentane 40:60 then 100:0) the product was recrystallized from dichloromethane and pentane to give orange crystals (0.91 g, 64%) of the all-trans isomer **14c**, mp 126−127 °C (by dsc). Anal. Calcd for $C_{15}H_{16}O_2S$: C, 69.20; H, 6.19; O, 12.39. Found: C, 69.2; H, 6.2; O, 12.3. ^{1}H NMR ($CDCl_3$) δ 9.58 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.16 (1 H, dd, H(3), $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 11.0 Hz); 7.09 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 7.03 (1 H, dd, H(b), $J_{a,b}$ = 1.5 Hz, $J_{b,c}$ = 8.0 Hz); 6.88 (1 H, s, H(a)); 6.85 (1 H, dd, H(6), $J_{5,6}$ = 10.5 Hz, $J_{6,7}$ = 15.0 Hz); 6.80 (1 H, dd, H(5), $J_{4,5}$ = 13.5 Hz, $J_{5,6}$ = 10.5 Hz); 6.74 (1 H, d, H(7), $J_{6,7}$ = 15.0 Hz); 6.54 (1 H, dd, H(4), $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 13.5 Hz); 6.17 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.5 Hz); 3.915 (3 H, s, OCH_3); 2.43 (3H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.2, 156.5, 151.4, 142.6, 138.0, 134.3, 131.1, 129.9, 129.1, 127.1, 125.8, 120.7, 107.9, 55.9, 14.6.

***(E,E,E)*-7-(3,4-Dimethoxyphenyl)hepta-2,4,6-trienal (13c).** Trienal **13c** was prepared from 3,4-dimethoxybenzaldehyde (**11**, 0.8 g, 4.8 mmol) and phosphonate **III** (1.66 g, 6 mmol) according to general procedure B. The crude product was chromatographed on silica gel (diethyl ether) and recrystallized from dichloromethane and pentane to give the all-trans isomer **13c** (0.82 g, 70%), as orange needles, mp 135 °C (by dsc). Anal. Calcd for $C_{15}H_{16}O_3$: C, 73.75; H, 6.60. Found: C, 73.9; H, 6.5. ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 7.5 Hz); 7.15 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.0 Hz); 6.99 (1 H, d, H(b), $J_{b,c}$ = 8.5 Hz); 6.98 (1 H, s, H(a)); 6.83 (1 H, d, H(c), $J_{b,c}$ = 8.5 Hz); 6.80−6.77 (2 H, m, H(5), H(6)); 6.75 (1 H, d, H(7)); 6.51 (1 H, m, H(4)); 6.15 (1 H, dd, H(2), $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 15.0 Hz); 3.895 (3 H, s, OCH_3); 3.88 (3 H, s, OCH_3). ^{13}C NMR ($CDCl_3$) δ 193.2, 151.7, 150.2, 149.4, 142.9, 138.3, 130.8, 129.6, 129.2, 126.0, 121.0, 111.5, 109.4, 56.01, 55.97.

***(E,E,E)*-7-(4-Butoxy-3-(methylthio)phenyl)hepta-2,4,6-trienal (15c′).** Trienal **15c′** was synthesized from aldehyde **10** (1 g, 4.5 mmol) and phosphonate **III** (1.6 g, 5.8 mmol) according to general procedure B. The crude product was purified by flash chromatography on silica gel (diethyl ether and pentane 40:60) to give orange crystals (0.98 g, 73%), mp 105−106 °C. The product was then recrystallized in CH_2Cl_2/pentane. Anal. Calcd for $C_{18}H_{22}O_2S$: C, 71.49; H, 7.33; O, 10.58. Found: C, 71.35; H, 7.3; O, 10.9. ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.20 (1 H, d, H(a), $J_{a,b}$ = 2.0 Hz); 7.19 (1 H, dd, H(b), $J_{a,b}$ = 2.0 Hz, $J_{b,c}$ = 8.5 Hz); 7.16 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.0 Hz); 6.78 (1 H, d, H(c), $J_{b,c}$ = 8.5 Hz); 6.84−6.70 (3 H, m, H(5), H(6) and H(7)); 6.515 (1 H, m, H(4)); 6.155 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.04 (2 H, t, OCH_2, J = 6.5 Hz); 2.44 (3 H, s, SCH_3); 1.81 (2 H, m, CH_2); 1.53 (2 H, m, CH_2); 0.97 (3 H, t, CH_3, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 193.5, 156.5, 152.0, 143.1, 138.0, 130.7, 129.4, 129.2, 128.2, 125.9, 125.2, 124.2, 111.0, 68.6, 31.2, 19.3, 14.6, 13.8.

***(E,E,E)*-7-(3-Butoxy-4-(methylthio)phenyl)hepta-2,4,6-trienal (14c′).** Compound **14c′** was obtained from aldehyde **9** (0.55 g, 2.4 mmol) and phosphonate **III** (0.82 g, 3.0 mmol) according to general procedure B. The crude product was purified by flash chromatography on silica gel (diethyl ether and pentane 60:40); two fractions were collected. The first, which was a mixture of stereoisomers, was treated with iodine in dichloromethane and the resulting all-trans product was combined with the second chromatographic fraction and recrystallized from a mixture of dichloromethane and pentane, to give orange crystals of **14c′** (0.53 g, 73%), mp 108−109 °C (by dsc). Anal. Calcd for $C_{18}H_{22}O_2S$: C, 71.49; H, 7.33; O, 10.58. Found: C, 71.7; H, 7.3; O, 10.5. ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.16 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.5 Hz); 7.05 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 7.01 (1 H, d, H(b), $J_{b,c}$ = 8.0 Hz); 6.87 (1 H, s, H(a)); 6.86−6.70 (2 H, m, H(5), H(6)); 6.73 (1 H, d, H(7), $J_{6,7}$ = 14.5 Hz); 6.53 (1 H, m, H(4)); 6.16 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.05 (2 H, t, OCH_2, J = 6.0 Hz); 2.41 (3 H, s, SCH_3); 1.82 (2 H, m, CH_2); 1.54 (2 H, m, CH_2); 0.98 (3 H, t, CH_3, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 193.4, 155.6, 151.8, 142.8, 138.2, 133.8, 130.9, 129.7, 129.5, 126.8, 125.0, 120.5, 108.5, 68.4, 31.2, 19.3, 14.3, 13.9.

***(E,E,E)*-7-(3-Butoxy-4-methoxyphenyl)hepta-2,4,6-trienal (13c′).** The product **13c′** was prepared from compound **11** (1 g, 4.8 mmol) and phosphonate **III** (1.66 g, 6 mmol) according to general procedure B. The product was purified by flash chromatography on silica gel (diethyl ether and pentane 70:30), affording orange crystals of **13c′** (0.82 g, 60%), mp 79−80 °C (by dsc). Anal. Calcd for $C_{18}H_{22}O_3$: C, 75.50; H, 7.74. Found: C, 75.2; H, 7.5. ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.155 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.5 Hz); 6.97 (2 H, m, H(a) and H(b)); 6.84−6.68 (4 H, m, H(5), H(6), H(7), and H(c)); 6.51 (1 H, m, H(4)); 6.145 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.03 (2 H, t, OCH_2, J = 7.0 Hz); 3.86 (3 H, s, OCH_3); 1.83 (2 H, m, CH_2); 1.49 (2 H, m, CH_2); 0.97 (3 H, t, CH_3, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 193.4, 152.0, 150.5, 148.8, 143.1, 138.4, 130.6, 129.4, 129.1, 125.8, 120.9, 111.6, 110.7, 68.8, 56.0, 31.2, 19.2, 13.9.

***(E,E,E,E)*-9-(4-Methoxy-3-(methylthio)phenyl)nona-2,4,6,8-tetraenal (15d).** The product **15d** was prepared from the dienal **15b** (0.63 g, 2.7 mmol) and phosphonate **II** (0.75 g, 3.0 mmol) according to general procedure B. The crude product was flash chromatographed on silica gel (dichloromethane) and isomerized in the presence of iodine in dichloromethane. Recrystallization from a mixture of dichloromethane and pentane afforded the desired all-trans **15d** (0.39 g, 50%) as red crystals, mp 171−172 °C (by dsc). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.29; H, 6.33; O, 11.17. Found: C, 71.1; H, 6.2; O, 11.1. MS *m/z* 286 (M^+, 100%), 210 (27%), 167 (28%), 115 (11%). ^{1}H NMR ($CDCl_3$) δ 9.55 (1 H, d, H(1), $J_{1,2}$ = 8.5 Hz); 7.235 (1 H, d, H(a), $J_{a,b}$= 2.0 Hz); 7.19 (1 H, dd, H(b), $J_{a,b}$ = 2.0 Hz, $J_{b,c}$ = 9.0 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.0 Hz); 6.79 (1 H, d, H(c), $J_{b,c}$ = 9.0 Hz); 6.75 (1 H, dd, H(8), $J_{8,9}$ = 15.5 Hz, $J_{7,8}$ = 11.0 Hz); 6.73 (1 H, dd, H(5), $J_{4,5}$ = 15.5 Hz, $J_{5,6}$ = 11.0 Hz); 6.63 (1 H, d, H(9), $J_{8,9}$ = 15.5 Hz); 6.61 (1 H, dd, H(7), $J_{6,7}$ = 15.5 Hz, $J_{7,8}$ = 11.0 Hz); 6.45 (1 H, dd, H(4), $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 15.5 Hz); 6.42 (1 H, dd, H(6), $J_{5,6}$ = 11.0 Hz, $J_{6,7}$ = 15.5 Hz); 6.15 (1 H, dd, H(2), $J_{2,3}$ = 15.0 Hz, $J_{1,2}$ = 8.5 Hz); 3.89 (3 H, s, OCH_3); 2.44 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.4, 156.6, 151.8, 142.8, 139.1, 135.5, 131.1, 130.8, 130.1, 129.5, 127.6, 126.7, 125.0, 124.4, 110.2, 56.0, 14.8.

***(E,E,E,E)*-9-(3-Methoxy-4-(methylthio)phenyl)nona-2,4,6,8-tetraenal (14d).** Compound **14d** was synthesized from the dienal **14b** (0.6 g, 2.6 mmol) and phosphonate **II** (0.75 g, 3.0 mmol) according to general procedure B. After purification by flash chromatography on silica gel (dichloromethane), a mixture of two stereoisomers was obtained, which was isomerized mainly to the all-trans isomer **14d** in the presence of iodine in dichloromethane; this compound was recrystallized from a mixture of dichloromethane and pentane to give red crystals of **14d** (0.38 g, 52%), mp 167 °C (by dsc). Anal. Calcd for $C_{17}H_{18}O_2S$: C, 71.29; H, 6.33; O, 11.17. Found: C, 71.2; H, 6.6; O, 11.1. MS *m/z* 286 (M^+, 100%), 210 (22%), 167 (20%). ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.13 (1 H, dd, H(3), $J_{3,4}$ = 11.5 Hz, $J_{2,3}$ = 15.0 Hz); 7.09 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 7.01 (1 H, dd, H(b), $J_{b,c}$ = 8.0 Hz, $J_{a,b}$ = 1.5 Hz); 6.87 (1 H, s, H(a)); 6.825 (1 H, dd, H(8), $J_{7,8}$ = 11.5 Hz, $J_{8,9}$ = 15.5 Hz); 6.74 (1 H, dd, H(5), $J_{4,5}$ = 15.0 Hz, $J_{5,6}$ = 11.5 Hz); 6.65 (1 H, d, H(9), $J_{8,9}$ = 15.5 Hz); 6.62 (1 H, dd, H(7), $J_{6,7}$ = 15.0 Hz, $J_{7,8}$ = 11.5 Hz); 6.46 (1 H, dd, H(4), $J_{3,4}$ = 11.5 Hz, $J_{4,5}$ = 15.0 Hz); 6.44 (1 H, dd, H(6), $J_{5,6}$ = 11.5 Hz, $J_{6,7}$ = 15.0 Hz); 6.15 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 3.91 (3 H, s, OCH_3); 2.42 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.15, 156.5, 151.4, 142.5, 138.8, 135.75, 134.8, 131.6, 131.0, 129.9, 128.3, 127.8, 126.0, 120.4, 107.8, 55.9, 14.7.

***(E,E,E,E)*-9-(3,4-Dimethoxyphenyl)nona-2,4,6,8-tetraenal (13d).** Compound **13d** was prepared from the dienal **13b** (0.6 g, 2.8 mmol) and phosphonate **II** (0.85 g, 3.4 mmol) according to general procedure B. The crude product was flash chromatographed on silica gel (dichloromethane) and recrystallized from a mixture of dichloromethane and pentane to give red crystals of the all-trans isomer **13d** (0.3 g, 40%), mp 176 °C (by dsc). Anal. Calcd for $C_{17}H_{18}O_3$: C, 75.53; H, 6.71. Found: C, 75.4; H, 6.6. MS *m/z* 270 (M^+, 100%), 241 (18%), 165 (19%), 115 (20%), 91 (18%), 77 (17%). ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.5 Hz); 6.97 (1 H, d, H(b), $J_{b,c}$ = 8.5 Hz); 6.96 (1 H, s, H(a)); 6.82 (1 H, d, H(c), $J_{b,c}$ = 8.5 Hz); 6.74 (1 H, dd, H(5), $J_{4,5}$ = 15.5 Hz, $J_{5,6}$ = 11.5 Hz); 6.735 (1 H, dd, H(8), $J_{7,8}$ = 11.5 Hz, $J_{8,9}$ = 15.5 Hz); 6.64 (1 H, d, H(9), $J_{8,9}$ = 15.5 Hz);

6.62 (1 H, dd, H(7), $J_{6,7}$ = 15.5 Hz, $J_{7,8}$ = 11.5 Hz); 6.45 (1 H, dd, H(4), $J_{3,4}$ = 11.5 Hz, $J_{4,5}$ = 15.5 Hz); 6.41 (1 H, dd, H(6), $J_{5,6}$ = 11.5 Hz, $J_{6,7}$ = 15.5 Hz); 6.15 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 3.90 (3 H, s, OCH_3); 3.88 (3 H, s, OCH_3). ^{13}C NMR ($CDCl_3$) δ 193.2, 151.55, 149.9, 149.4, 142.7, 139.1, 136.0, 131.0, 130.8, 130.1, 129.5, 126.7, 120.6, 111.6, 109.3, 56.03, 55.98.

(*E*,*E*,*E*,*E*,*E*)-11-(4-Methoxy-3-(methylthio)phenyl)undeca-2,4,6,8,10-pentaenal (15e). This compound was prepared from the dienal **15b** (0.84 g, 3.6 mmol) and phosphonate **III** (1.24 g, 4.5 mmol).The crude product was flash chromatographed under argon on a short column of silica gel (dichloromethane) to give a mixture of stereoisomers (0.67 g, 60%, >90% of the all-trans isomer). Recrystallization from a mixture of dichloromethane and pentane gave the pure all-trans compound **15e**, dark red crystals, mp 203−204 °C (by dsc). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; O, 10.24. Found: C, 72.8; H, 6.5; O, 10.0. MS *m*/*z* 312 (M^+, 100%), 167 (49%). ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.22 (1 H, s, H(a)); 7.18 (1 H, d, H(b), $J_{b,c}$ = 8.5 Hz); 7.12 (1 H, dd, H(3), $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 11.5 Hz); 6.78 (1 H, d, H(c), $J_{b,c}$ = 8.5 Hz); 6.74 (1 H, dd, H(10), $J_{9,10}$ = 10.5 Hz, $J_{10,11}$ = 15.5 Hz); 6.71 (1 H, dd, H(5), $J_{4,5}$ = 15.0 Hz, $J_{5,6}$ = 11.0 Hz); 6.58 (1 H, d, H(11), $J_{10,11}$ = 15.5 Hz); 6.55 (1 H, dd, H(7), $J_{6,7}$ = 15.0 Hz, $J_{7,8}$ = 11.0 Hz); 6.52 (1 H, dd, H(9), $J_{8,9}$ = 15.0 Hz, $J_{9,10}$ = 10.5 Hz); 6.44 (1 H, dd, H(4), $J_{3,4}$ = 11.5 Hz, $J_{4,5}$ = 15.0 Hz); 6.40 (1 H, dd, H(8), $J_{7,8}$ = 11.0 Hz, $J_{8,9}$ = 15.0 Hz); 6.36 (1 H, dd, H(6), $J_{5,6}$ = 11.0 Hz, $J_{6,7}$ = 15.0 Hz); 6.14 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.5 Hz); 3.89 (3 H, s, OCH_3); 2.44 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.4, 156.5, 151.8, 142.75, 139.0, 136.95, 134.2, 131.9, 131.3, 130.8, 130.4, 129.7, 127.5, 127.1, 124.8, 124.3, 110.2, 56.0, 14.85.

(*E*,*E*,*E*,*E*,*E*)-11-(3-Methoxy-4-(methylthio)phenyl)undeca-2,4,6,8,10-pentaenal (14e). Compound **14e** was synthesized from the dienal **14b** (0.84 g, 3.6 mmol) and phosphonate **III** (1.24 g, 4.5 mmol). The crude product was flash chromatographed under argon on a short column on silica gel (dichloromethane) to give a mixture of stereoisomers (0.78 g, 69%, >90% of the all-trans isomer). Recrystallization from a mixture of dichloromethane and pentane gave the pure all-trans compound **14e**, dark red crystals, mp 196−197 °C (by dsc). Anal. Calcd for $C_{19}H_{20}O_2S$: C, 73.04; H, 6.45; O, 10.24. Found: C, 72.9; H, 6.4; O, 10.3. MS *m*/*z* 312 (M^+, 100%), 167 (42%). ^{1}H NMR ($CDCl_3$) δ 9.56 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.12 (1 H, dd, H(3), $J_{2,3}$ = 15.5 Hz, $J_{3,4}$ = 11.5 Hz); 7.08 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 6.99 (1 H, dd, H(b), $J_{a,b}$ = 1.5 Hz, $J_{b,c}$ = 8.0 Hz); 6.86 (1 H, d, H(a), $J_{a,b}$ = 1.5 Hz); 6.81 (1 H, dd, H(10), $J_{9,10}$ = 11.0 Hz, $J_{10,11}$ = 15.0 Hz); 6.715 (1 H, dd, H(5), $J_{4,5}$ = 15.0 Hz, $J_{5,6}$ = 11.5 Hz); 6.59 (1 H, d, H(11), $J_{10,11}$ = 15.0 Hz); 6.56 (1 H, dd, H(7), $J_{6,7}$ = 15.0 Hz, $J_{7,8}$ = 11.0 Hz); 6.53 (1 H, dd, H(9), $J_{8,9}$ = 15.0 Hz, $J_{9,10}$ = 11.0 Hz); 6.45 (1 H, dd, H(4), $J_{3,4}$ = 11.5 Hz, $J_{4,5}$ = 15.0 Hz); 6.42 (1 H, dd, H(8), $J_{7,8}$ = 11.0 Hz, $J_{8,9}$ = 15.0 Hz); 6.37 (1 H, dd, H(6), $J_{5,6}$ = 11.5 Hz, $J_{6,7}$ = 15.0 Hz); 6.15 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.5 Hz); 3.91 (3 H, s, OCH_3); 2.42 (3 H, s, SCH_3). ^{13}C NMR ($CDCl_3$) δ 193.4, 156.3, 151.7, 142.6, 138.8, 136.7, 134.95, 134.5, 132.4, 131.65, 130.9, 129.9, 128.1, 127.7, 125.75, 120.2, 107.4, 55.8, 14.6.

(*E*,*E*,*E*,*E*,*E*)-11-(3,4-Dimethoxyphenyl)undeca-2,4,6,8,10-pentaenal (13e). Phosphonate **III** (0.95 g, 3.4 mmol) and dienal **13b** (0.6 g, 2.8 mmol) were used as starting materials for the preparation of **13e**. The crude product was flash chromatographed under argon on a short column of silica gel (dichloromethane) to give a mixture of stereoisomers (0.49 g, 61%, >90% of the all-trans isomer). Concentration of a dichloromethane solution gave brown crystals of the pure all-trans compound **13e**, which was isolated by suction filtration, washed with a small amount of dichloromethane and diethyl ether, and dried in vacuum; 204−205 °C (dec, by dsc). Anal. Calcd for $C_{19}H_{20}O_3$: C, 77.00; H, 6.80. Found: C, 76.9; H, 6.8. MS *m*/*z* 296 (M^+, 100%), 151 (64%), 91 (30%). ^{1}H NMR ($CDCl_3$) δ 9.55 (1 H, d, H(1), $J_{1,2}$ = 7.5 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.0 Hz); 6.95 (1 H, dd, H(b), $J_{a,b}$ = 1.5 Hz, $J_{b,c}$ = 9.0 Hz); 6.94 (1 H, s, H(a)); 6.81 (1 H, d, H(c), $J_{b,c}$ = 9.0 Hz); 6.74 (1 H, dd, H(10), $J_{9,10}$ = 11.0 Hz, $J_{10,11}$ = 15.0 Hz); 6.72 (1 H, dd, H(5), $J_{4,5}$ = 15.0 Hz, $J_{5,6}$ = 11.0 Hz); 6.58 (1 H, d, H(11), $J_{10,11}$ = 15.0 Hz); 6.56 (1 H, dd, H(7), $J_{6,7}$ = 15.0 Hz, $J_{7,8}$ = 11.0 Hz); 6.53 (1 H, dd, H(9), $J_{8,9}$ = 15.0 Hz, $J_{9,10}$ = 11.0 Hz); 6.45 (1 H, dd, H(4), $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 15.0 Hz); 6.40 (1 H, dd, H(8), $J_{7,8}$ = 11.0 Hz, $J_{8,9}$ = 15.0 Hz); 6.36 (1 H, dd, H(6), $J_{5,6}$ = 11.0 Hz, $J_{6,7}$ = 15.0 Hz); 6.14 (1 H, dd, H(2), $J_{1,2}$ = 7.5 Hz, $J_{2,3}$ = 15.0 Hz); 3.90 (3 H, s, OCH_3); 3.88 (3 H, s, OCH_3). ^{13}C NMR ($CDCl_3$) δ 193.4, 151.8, 149.4, 149.2, 142.8, 139.0, 137.0, 134.7, 131.7, 131.25, 130.8, 130.2, 129.65, 126.95, 120.3, 111.2, 108.7, 55.95, 55.86.

(*E*,*E*,*E*,*E*,*E*)-11-(3-Butoxy-4-methoxyphenyl)undeca-2,4,6,8,10-pentaenal (13e′). Compound **13e** was prepared from phosphonate **III** (0.97 g, 3.5 mmol) and dienal **13b′** (0.72 g, 2.8 mmol). The crude product was flash chromatographed under argon on a short column of silica gel (dichloromethane) to give a mixture of stereoisomers (0.47 g, 50%, mostly consisting of the all-trans isomer). Recrystallization from a mixture of dichloromethane and pentane gave the pure all-trans isomer **13e′**, red crystals, mp 155 °C (by dsc). Anal. Calcd for $C_{22}H_{26}O_3$: C, 78.08; H, 7.74. Found: C, 78.05; H, 7.8. ^{1}H NMR ($CDCl_3$) δ 9.545 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.0 Hz); 6.95 (1 H, s, H(a)); 6.94 (1 H, d, H(b), $J_{b,c}$ = 8.0 Hz); 6.81 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 6.72 (2 H, 2 dd, H(5) and H(10), $J_{4,5}$ = 15.0 Hz, $J_{5,6}$ = 11.0 Hz, $J_{9,10}$ = 11.0 Hz, $J_{10,11}$ = 15.5 Hz); 6.57 (1 H, d, H(11), $J_{10,11}$ = 15.5 Hz); 6.52 (2 H, 2 dd, H(7) and H(9), $J_{6,7}$ = 15.0 Hz, $J_{7,8}$ = 11.0 Hz, $J_{8,9}$ = 15.0 Hz, $J_{9,10}$ = 11.0 Hz); 6.44 (1 H, dd, H(4), $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 15.0 Hz); 6.39 (1 H, dd, H(8), $J_{7,8}$ = 11.0 Hz, $J_{8,9}$ = 15.0 Hz); 6.35 (1 H, dd, H(6), $J_{5,6}$ = 11.0 Hz, $J_{6,7}$ = 15.0 Hz); 6.13 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.03 (2 H, t, OCH_2, J = 6.5 Hz); 3.85 (3 H, s, OCH_3); 1.89 (2 H, m, CH_2); 1.495 (2 H, m, CH_2); 0.97 (3 H, t, CH_3, J = 7,5 Hz). ^{13}C NMR ($CDCl_3$) δ 193.4, 151.8, 149.85, 148.8, 142.8, 139.1, 137.1, 134.8, 131.6, 131.2, 130.7, 130.1, 129.6, 126.8, 120.3, 111.6, 110.45, 68.7, 56.0, 31.25, 19.2, 13.9.

(*E*,*E*,*E*,*E*,*E*)-11-(3-Butoxy-4-(methylthio)phenyl)undeca-2,4,6,8,10-pentaenal (14e′). Phosphonate **III** (0.69 g, 2.5 mmol) and dienal **14b′** (0.55 g, 2 mmol) were used as starting materials for the preparation of pentaenal **14e′**. The crude product was flash chromatographed under argon on a short column of silica gel (dichloromethane) to give a mixture of stereoisomers (0.41 g, 58%, mostly consisting of the all-trans isomer). Recrystallization from a mixture of dichloromethane and pentane gave the pure all-trans compound **14e′**, as red crystals, mp 164−165 °C (by dsc). Anal. Calcd for $C_{22}H_{26}O_2S$: C, 74.54; H, 7.39; O, 9.03. Found: C, 74.3; H, 7.3; O, 9.1. ^{1}H NMR ($CDCl_3$) δ 9.55 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.0 Hz); 7.04 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 6.97 (1 H, d, H(b), $J_{b,c}$ = 8.0 Hz); 6.85 (1 H, s, H(a)); 6.80 (1 H, dd, H(10), $J_{9,10}$ = 11.0 Hz, $J_{10,11}$ = 15.5 Hz); 6.72 (1 H, dd, H(5), $J_{4,5}$ = 14.5 Hz, $J_{5,6}$ = 11.5 Hz); 6.58 (1 H, d, H(11), $J_{10,11}$ = 15.5 Hz); 6.55 (1 H, dd, H(7), $J_{6,7}$ = 15.0 Hz, $J_{7,8}$ = 11.0 Hz); 6.53 (1 H, dd, H(9), $J_{8,9}$ = 15.0 Hz, $J_{9,10}$ = 11.0 Hz); 6.45 (1 H, dd, H(4), $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 14.5 Hz); 6.42 (1 H, dd, H(8), $J_{7,8}$ = 11.0 Hz, $J_{8,9}$ = 15.0 Hz); 6.365 (1 H, dd, H(6), $J_{5,6}$ = 11.5 Hz, $J_{6,7}$ = 15.0 Hz); 6.14 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.05 (2 H, t, OCH_2, J = 6.5 Hz); 2.41 (3 H, s, SCH_3); 1.82 (2 H, m, CH_2); 1.53 (2 H, m, CH_2); 0.98 (3 H, t, CH_3, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 193.4, 155.7, 151.7, 142.7, 138.9, 136.8, 134.6 (2C), 132.3, 131.55, 130.8, 129.8, 128.2, 127.9, 125.3, 120.0, 108.4, 68.4, 31.25, 19.3, 14.4, 13.9.

(*E*,*E*,*E*,*E*,*E*,*E*)-13-(4-Butoxy-3-(methylthio)phenyl)trideca-2,4,6,8,10,12-hexaenal (15f′). Trienal **15e′** (0.7 g, 2.3 mmol) and phosphonate **III** (0.8 g, 2.9 mmol) were used as starting materials to prepare hexaenal **15f′**. The crude product was flash chromatographed under argon on a short column of silica gel (dichloromethane) to give a mixture of stereoisomers (0.48 g, 55%, mostly consisting of the all-trans isomer). Recrystallization from a mixture of dichloromethane and pentane gave the pure all-trans compound **15f′**, as dark brown crystals, 200 °C (dec, by dsc). Anal. Calcd for $C_{24}H_{28}O_2S$: C, 75.75; H, 7.42; O, 8.41. Found: C, 75.2; H, 7.3; O, 8.5. HRMS *m*/*z* calcd 380.1810, found 380.1810. ^{1}H NMR ($CDCl_3$) δ 9.55 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.17 (1 H, d, H(a), $J_{a,b}$ = 1.5 Hz); 7.14 (1 H, d, H(b), $J_{b,c}$ = 8.5 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.0 Hz); 6.76 (1 H, d, H(c), $J_{b,c}$ = 8.5 Hz); 6.73

(1 H, dd, H(12), $J_{11,12}$ = 11.0 Hz, $J_{12,13}$ = 15.0 Hz); 6.71 (1 H, dd, H(5), $J_{4,5}$ = 15.0 Hz, $J_{5,6}$ = 11.0 Hz); 6.54 (1 H, d, H(13), $J_{12,13}$ = 15.0 Hz); 6.53−6.30 (7 H, m, H(4), H(6), H(7), H(8), H(9), H(10), H(11)); 6.14 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.03 (2 H, t, OCH_2, J = 6.5 Hz); 2.43 (3 H, s, SCH_3); 1.80 (2 H, m, CH_2); 1.51 (2 H, m, CH_2); 0.97 (3 H, t, CH_3, J = 7.5 Hz). ^{13}C NMR ($CDCl_3$) δ 193.4, 155.8, 151.75, 142.8, 139.0, 136.9, 135.8, 133.6, 132.2, 132.1, 131.4, 130.8, 130.3, 129.7, 127.8, 127.2, 124.5, 123.9, 111.1, 68.6, 31.2, 19.3, 14.7, 13.85.

(*E*,*E*,*E*,*E*,*E*)-13-(3-Butoxy-4-(methylthio)phenyl)trideca-2,4,6,8,10,12-hexaenal (14f′). Hexaenal **14f′** was prepared from phosphonate **III** (0.4 g, 1.44 mmol) and trienal **14c′** (0.35 g, 1.15 mmol). The crude product was flash chromatographed under argon on a short column of silica gel (dichloromethane) to give a mixture of stereoisomers (0.23 g, 52%, mostly consisting of the all-trans isomer). Recrystallization from a mixture of dichloromethane and pentane gave dark brown crystals of the pure all-trans compound **14f′**, which was washed with diethyl ether and dried in vacuum; 199−200 °C (dec, by dsc). Anal. Calcd for $C_{24}H_{28}O_2S$: C, 75.75; H, 7.42; O, 8.41. Found: C, 76.0; H, 7.5; O, 8.4. MS *m*/*z* 380 (M^+, 100%), 153 (28%). ^{1}H NMR ($CDCl_3$) δ 9.55 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.5 Hz); 7.04 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 6.97 (1 H, d, H(b), $J_{b,c}$ = 8.0 Hz); 6.84 (1 H, s, H(a)); 6.79 (1 H, dd, H(12), $J_{11,12}$ = 10.5 Hz, $J_{12,13}$ = 15.5 Hz); 6.71 (1 H, dd, H(5), $J_{4,5}$ = 14.5 Hz, $J_{5,6}$ = 11.5 Hz); 6.55 (1 H, d, H(13), $J_{12,13}$ = 15.5 Hz); 6.54 (1 H, m, H(7)); 6.50−6.30 (6 H, m, H(4), H(6), H(8), H(9), H(10), H(11)); 6.14 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.04 (2 H, t, OCH_2, J = 6.5 Hz); 2.41 (3 H, s, SCH_3); 1.82 (2 H, m, CH_2); 1.54 (2 H, m, CH_2); 0.98 (3 H, t, CH_3, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 193.4, 155.8, 151.7, 142.7, 138.9, 136.8, 135.6, 134.9, 133.8, 132.7, 132.4, 131.6, 130.8, 129.8, 128.15, 127.9, 125.4, 119.9, 108.4, 68.4, 31.3, 19.3, 14.5, 13.9.

(*E*,*E*,*E*,*E*,*E*)-13-(3-Butoxy-4-methoxyphenyl)trideca-2,4,6,8,10,12-hexaenal (13f′). Trienal **13c′** (0.55 g, 1.9 mmol) and phosphonate **III** (0.66 g, 2.4 mmol) were used as starting materials to prepare hexaenal **13f′**. The crude product was flash chromatographed under argon on a short column of silica gel (dichloromethane) to give a mixture of stereoisomers (0.27 g, 40%, mostly consisting of the all-trans isomer). Recrystallization from a mixture of dichloromethane and pentane gave dark brown crystals of the pure all-trans compound **13f′**, 195−196 °C (dec, by dsc). Anal. Calcd for $C_{24}H_{28}O_3$: C, 79.09; H, 7.74. Found: C, 78.9; H, 7.8. MS *m*/*z* 364 (M^+, 100%), 193 (12%). ^{1}H NMR ($CDCl_3$) δ 9.55 (1 H, d, H(1), $J_{1,2}$ = 8.0 Hz); 7.13 (1 H, dd, H(3), $J_{2,3}$ = 15.0 Hz, $J_{3,4}$ = 11.5 Hz); 6.94 (1 H, s, H(a)); 6.93 (1 H, d, H(b), $J_{b,c}$ = 8.0 Hz); 6.80 (1 H, d, H(c), $J_{b,c}$ = 8.0 Hz); 6.71 (2 H, 2 dd, H(5), H(12), $J_{4,5}$ = 15.0 Hz, $J_{5,6}$ = 11.0 Hz, $J_{11,12}$ = 11.0 Hz, $J_{12,13}$ = 15.0 Hz); 6.58−6.41 (4 H, m, H(7), H(9), H(11)); 6.54 (1 H, d, H(13), $J_{12,13}$ = 15.5 Hz); 6.44 (1 H, dd, H(4), $J_{3,4}$ = 11.0 Hz, $J_{4,5}$ = 15.0 Hz); 6.41−6.30 (3 H, m, H(6), H(8), H(10)); 6.135 (1 H, dd, H(2), $J_{1,2}$ = 8.0 Hz, $J_{2,3}$ = 15.0 Hz); 4.03 (2 H, t, OCH_2, J = 6.5 Hz); 3.85 (3 H, s, OCH_3); 1.83 (2 H, m, CH_2); 1.50 (2 H, m, CH_2); 0.97 (3 H, t, CH_3, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ 193.45, 151.85, 149.6, 148.7, 142.8, 139.1, 136.95, 135.9, 134.0, 132.0, 131.98, 131.4, 130.7, 130.2, 129.7, 127.0, 120.1, 111.55, 110.3, 68.7, 56.0, 31.2, 19.2, 13.9.

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