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Second Order Hyperpolarisabilities of Various Series of Organic Compounds: Tetrathiafulvalene Derivatives

Introduction

Nonlinear interaction between light and matter gives rise to new optical phenomena which depend on the light intensity and in which the principle of light waves interactions is not valid. If the electric polarization vector of a material medium can be represented in a form of a power series with respect to succesive powers of the electric field amplitude, different optical phenomena are connected with each term of this expansion. Besides the fundamental importance for the understanding of physical mechanisms in the matter-strong laser field interactions, the research in nonlinear optics have led to numerous important applications. These present and potential applications motivate extensive search for new effective materials for nonlinear optics, i.e., materials presenting large nonlinear response to the external optical field, weak absorption losses and short response time. In these investigations an important role is played by different organic compounds which can possess large optical nonlinearities, are chemically flexible and can be prepared in acetylenic and ethylenic forms [1–5].

The nonlinear optical properities have been observed in molecules with highly delocalized π electrons, in which the chain of conjugated bonds facilitates the polarization of the molecule in external field. In particular, the organic conjugated molecules can present third-order nonlinearities [6–12].

In the present article a brief review is given of recent investigations on the third-order nonlinear optical properties of new tetrathiafulvalene (TTF) derivatives. TTF derivatives are precursors of organic metals presenting remarkable conducting properties [13]. Their extended molecular structure promote the occurence of delocalized π electrons owing to a presence of a long system of conjugated bonds and a number of heterocyclic rings. These properties suggest that TTF derivatives may be compounds with large nonlinear responses.

The investigations described here were carried on in Laboratoire POMA (Propriétés Optiques des Materiaux et Applications), Equipe Photonique de Puissance (UMR CNRS 6136) and the compounds studied were synthesized in Laboratoire d'Ingénierie Moléculaire et Matériaux Organiques of University of Angers.

Third-order nonlinear susceptibility

The nonlinear optical properties of the matter are connected with the fact that the electric polarization vector **P** of the sample is a nonlinear function of the electric field **E** of the electromagnetic wave propagating in a medium. In general, the quantum mechanical analysis based on the microscopic model of the matter constituting the medium is necessary to analyze the response of a medium to an external electromagnetic field. This is a very difficult task and in practice various approximation methods are used in different physical situations. The standard approach to consider the phenomena in nonlinear optics is to expand an unknown function **P** = **P**(**E**) into a power series of **E**:

$$P_i = P_i^{<1>} + P_i^{<2>} + P_i^{<3>} + \ldots = \chi_{ij}^{<1>} E_j + \chi_{ijk}^{<2>} E_j E_k + \chi_{ijkl}^{<3>} E_j E_k E_l + \ldots \tag{1}$$

where the indices indicate the components x, y, z and the Einstein's summation convention has been used. It is a kind of a perturbative approach which introduces the concept of nonlinear susceptibility of the medium. The terms of this expansion describe the nonlinear phenomena of the corresponding order [14,15]. The coefficients $\chi^{<n>}$ are defined as the electrical (optical) susceptibilities of order „n" and their detailed description can be found in classical textbooks on the subject; here we limit ouerselves to a brief presentation of those properties of the third order susceptibility which are important for the following discussion.

The object of research described in the present review was the third-order nonlinear optical properties of a family of new organic materials characterized by the nonresonant third order nonlinear optical susceptibility tensor $\chi^{<3>}$. The $\chi^{<3>}$ is in general a complex quantity, the imaginary part of which is related to the nonlinear absorption of radiation. The studied molecules presented only linear absorption (with one exception which will be commented upon separately) and thus $\mathrm{Im}\chi^{<3>} = 0$.

In all experiments the picosecond laser pulses were used. Two essential physical mechanisms contribute to the nonlinearities in isotropic materials interacting with radiation pulses of this duration: deformations of the electronic cloud and reorientation of the molecule. The much slower ($> 10^{-9}$ s) thermal and electrostrictive effects can be neglected. If, moreover, the laser frequency is nonresonant (in the case of molecules studied their absorption spectra revealed the existence of the absorption bands corresponding to the wavelengths much shorter than $\lambda = 532$ nm of the laser wave), the $\chi^{<3>}$ can be considered as being composed of two contributions corresponding to the two mechanisms mentioned above:

$$\chi^{<3>} = \chi^{<3>\,\mathrm{el}} + \chi^{<3>\mathrm{nucl}} \tag{2}$$

$\chi^{<3>\,\mathrm{el}}$ is called the electronic and $\chi^{<3>\mathrm{nucl}}$ the nuclear (or molecular) components of the susceptibility. In isotropic media (which was the case of our samples prepared in the form of solutions) the electronic and nuclear components satisfy the following relations [16,17]:

$$\chi_{xxxx}^{<3>\,\mathrm{el}} = 3\chi_{xxyy}^{<3>\,\mathrm{el}} = 3\chi_{yxyx}^{<3>\,\mathrm{el}} = 3\chi_{yxxy}^{<3>\,\mathrm{el}} \tag{3.1}$$

$$\chi_{xxxx}^{<3>\,\mathrm{nucl}} = 8\chi_{xxyy}^{<3>\,\mathrm{nucl}} = 8\chi_{yxyx}^{<3>\,\mathrm{nucl}} = \frac{4}{3}\chi_{yxxy}^{<3>\,\mathrm{nucl}} \tag{3.2}$$

Experimental results concerning the values of the components of $\chi^{<3>}$ together with relations (3) will thus allow us to determine the values of both the electronic and nuclear contributions to the susceptibility.

The susceptibility tensor characterizes nonlinear optical response of the dielectric material on the macroscopic level. The physical quantity that characterizes optical nonlinearities of an individual molecule is its second hyperpolarizability γ. In the case of solutions one obtains the following relation between the susceptibility $\chi^{<3>}$ of a solution and hyperpolarizability γ of an molecule [8]:

$$\chi^{<3>} = F^4 N\gamma + \chi^{<3>}_{solvent} \tag{4}$$

where $F = (n^2 + 2)/3$ is the so-called Lorentz local field factor, $N = N_a C/M$ is the number of dissolved molecules per unity volume, M and C are, respectively, their molar mass and concentration, N_A is the Avogadro number, and n is the refractive coefficient of a medium. In our experiments $\chi^{<3>}_{solvent}$ was negligibly small.

Method of measuring the third-order susceptibility

To measure the third-order susceptibilities we used the degenerate four wave mixing method (DFWM) [15]. The idea of DFWM is shown in figure 1.

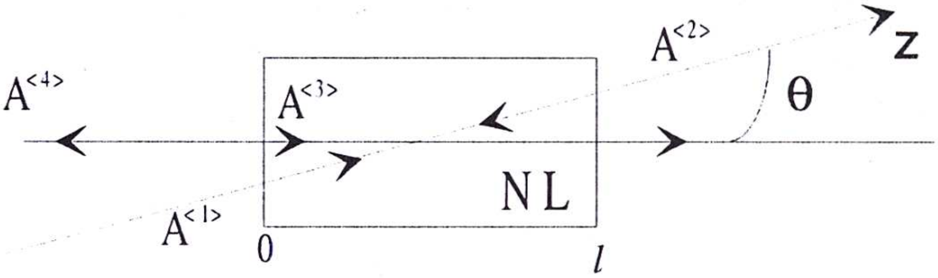


Fig. 1. Schematic diagram of the geometry of the light beams in an four wave mixing experiment

The nonlinear medium is irradiated by three waves of frequency ω: two of them are strong counterpropagating beams travelling in opposite directions („pump beams"), the third one („a probe beam") is a much weaker beam which makes a small angle (12° in our experiments) with respect to the direction of the pumps. The nonlinear polarization of the medium contains thus a component which is the source of the fourth wave („a signal wave") of the same frequency ω and propagating in a direction backward to the probe beam. In DFWM experiment the intensities of the light beams satisfied the relations: $I^{<1>}(z = 0) = I^{<2>}(z = l)$ and $I^{<3>}, I^{<4>} << I^{<1>}$. The important characteristic of the DFWM process is its efficiency defined as:

$$R = I^{<4>}(z = 0)/I^{<3>}(z = 0) \tag{5}$$

In general, the waves' amplitudes and thus the value of R, depend on polarizations of the beams and one should write R_{ijkl} instead of R to indicate that the polarization states of waves <4>, <1>, <2> and <3> are i, j, k and l, respectively, with indices taking values x or y. To simplify the notation we will omit the corresponding polarization indices in the following formulas and present only the general idea of a theoretical model. A more general form of the system of Eqs. (6) taking into account arbitrary polarizations of the beams can be found in [18].

To interprete the experimental results and determine the third-order susceptibility one compares the measured values of R with those calculated in the frame of a model based on the nonlinear propagation equations [15]. The laser waves propagating in the medium are taken as plane waves $\mathbf{E}^{<i>}(\mathbf{r},t) = \mathbf{A}^{<i>}(\mathbf{r})\exp[i(\mathbf{k}_i\mathbf{r} - \omega_i t)] + \text{c.c.}$ $(i = 1,2,3,4)$. Using the slowly varying amplitude approximation and assuming that all three incident waves are linearly polarized along the x axis, one obtains the following equations describing the waves propagation in the medium (in cgs units):

$$\begin{cases} \dfrac{\partial A_1}{\partial z} = -\dfrac{\alpha}{2}A_1 + iH\chi^{<3>}(A_1A_1^* + 2A_2A_2^*)A_1 \\ \dfrac{\partial A_2}{\partial z} = \dfrac{\alpha}{2}A_2 - iH\chi^{<3>}(2A_1A_1^* + A_2A_2^*)A_2 \\ \dfrac{dA_3}{dz} = -\Phi A_3 + 2iH\chi^{<3>}A_1A_2A_4^* \\ \dfrac{dA_4}{dz} = \Phi A_4 - 2iH\chi^{<3>}A_1A_2A_3^* \end{cases} \qquad (6)$$

where $A_i = A_x^{<i>}$, $\chi^{<3>} = \chi_{xxxx}^{<3>}$, $H = 12\pi^2/n\lambda$, $\Phi = \dfrac{\alpha}{2} - 2iH\chi^{<3>}(A_1A_1^* + A_2A_2^*)$, n is the linear refractive coefficient of the material, λ is the wavelength of the laser light and α is the linear absorption coefficient. The intensity of the beam is now $I_i = (nc/2\pi)A_iA_i^*$.

If the medium shows only linear absorption the third-order susceptibility is a real value and the above system can be solved to give the DFWM efficiency (reflectivity):

$$R = \frac{I^{<4>}(0)}{I^{<3>}(0)} = \begin{cases} \dfrac{p^2 + \dfrac{\alpha^2}{4}}{\left[p(\mathrm{ctg}(pl)) + \dfrac{\alpha}{2}\right]^2} & p^2 \geq 0 \\ \\ \dfrac{p^2 + \dfrac{\alpha^2}{4}}{\left[q(\mathrm{ctgh}(ql)) + \dfrac{\alpha}{2}\right]^2} & p^2 < 0 \end{cases} \tag{7}$$

where $p^2 = \left(\dfrac{48\pi^3}{n^2 c\lambda}\chi^{<3>}\right)^2 I^{<1>}(0)^2 \exp(-\alpha l) - \dfrac{\alpha^2}{4}$, $q = ip$. A general discussion of this model and its validity limits, taking into account linear and nonlinear absorption, was recently presented [19]. The values of the third-order susceptibility $\chi^{<3>}$ can be obtained by adjustment of the theoretical curve given by Eq. (7) to the experimantally measured values of the efficiency R.

In the DFWM experiments described here the samples were prepared in a form of solutions of powdered organic materials dissolved in chloroform or tetrahydro-furan. The thickness of the cell containing the sample was $l = 10^{-3}$ m. Excitation was provided by a 30-ps laser pulses at $\lambda = 532$ nm generated by an amplified mode-locked Quantel Nd:YAG laser operating at a 1 Hz repetition rate. The first step of the experimental procedure was the measurement of the intensity of the signal wave $I^{<4>}$ for several solution concentrations to determine the concentration for which $I^{<4>}$ is maximal. This concentration is called optimal, C_{opt}. All the compounds display the same kind of behavior, namely the existence of a single maximum of $I^{<4>}$. The intensity of the signal decreases when the concentration is larger than C_{opt} because of the competition between the generation of nonlinear polarization (characterized by $\chi^{<3>}$) and the absorption of radiation in the sample (characterized by α). The analysis of transmission for the range of the pump intensities up to 1.2 GW/cm^2 shows that molecules studied have linear absorption. Taking into account the values of the absorption coefficient at C_{opt} and of the efficiency R of the four wave mixing one can use Eq. (7) to deduce the values of $\chi^{<3>}$ which is the only free parameter in this equation. The efficiency R at C_{opt} was measured as a function of the intensity of wave <1> (in all experiments $I^{<3>} = 0.01\ I^{<1>}$) for different polarizations of waves <1>, <2> and <3>. Figure 2 presents an example (for the compound *e6*) of these results: R_{xxxx} versus $I^{<1>}$

in the case of vertical polarizations of incident beams; all the materials studied exhibit similar behavior.

A good agreement between experimental results and the theoretical curve given by Eq. (7) is observed in all cases. The adjustment of the theoretical curve to the experimental data allows us to deduce the values of different components of $\chi^{<3>}$.

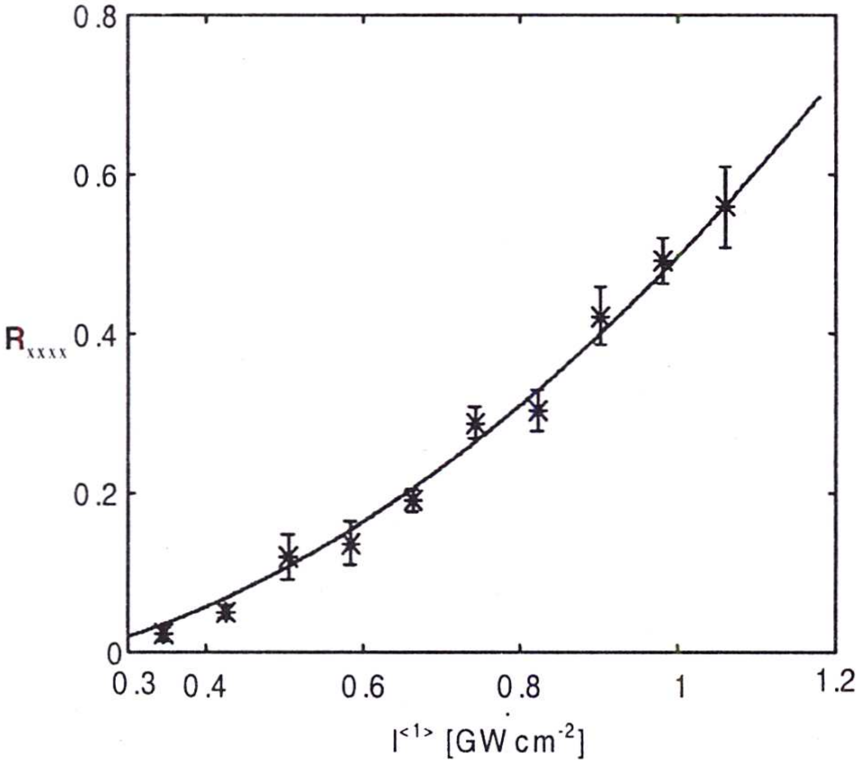


Fig. 2. Experimental values of the degenerate four wave mixing efficiency R_{xxxx} as a function of the intensity of the pump beam <1>. Polarizations of the incident waves <1>, <2> and <3> are all parallel to the x axis. $C_{opt} = 3$ g/dm^3. Continuous curve corresponds to the formula given by Eq. (7). (cf. [20])

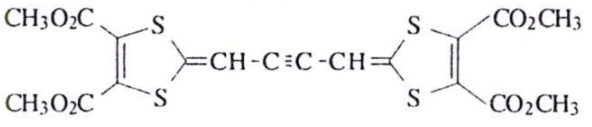
When the values of $\chi_{ijkl}^{<3>}$ are known, one can establish the numerical relationships between different tensor components. These results, together with the relations (3) allow one to deduce the values of the electronic and nuclear contributions to the total value of susceptibility. Moreover, one can obtain the values of the molecular hyperpolarizability using the formula (4).

Results

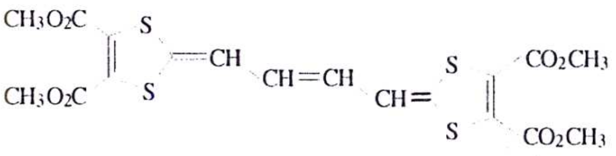
We have performed a systematic study of nonlinear optical properties of five new groups of tetrathiafulvalene derivatives. The characteristic property of these molecules is that their structures promote the occurence of a fully delocalized π electrons over the extended framework which makes them easily polarizable and, in consequence, makes them suitable candidates to reveal large opticale nonlinearities. This is due to the presence of a long system of: conjugated bonds and/or a number of heterocyclic rings that effectively „extend" the system. On the other hand, their response to the external electric fields depends on the details of the structure, such as a type of bond or substituents.

The figures and tables below present in a condensed form the results of a study of the third-order nonlinear optical properties of these molecules, a detailed presentation may be found in original papers quoted below. The following groups of TTF derivatives were examined: acetylenic derivatives [21], ethylenic derivatives [20], bisdithiafulvenyl-substituted derivatives [22], polyfluoroalkylsulfanyl-substituted derivatives[23] and p-N,N'-dimethylaniline derivatives [18]. In the columns of all tables are shown: the linear absorption coefficient α, the measured absolute value of the third order susceptibility $\chi^{<3>}_{xxxx}$, the so-called merit factor $\chi^{<3>}_{xxxx}/\alpha$ which characterizes the „ratio" between two competing physical processes in a sample.

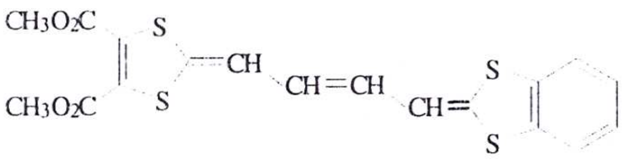
The effectiveness of the wave mixing and the absorption of radiation, and, in the last column,the absolute value of the electronic contribution to second-order molecular polarizability γ^{el}. The value of the second-order hyperpolarizability of CS_2 which is the reference material for DFWM measurements is 4.71×10^{49} [m^5V^{-2}] [15].



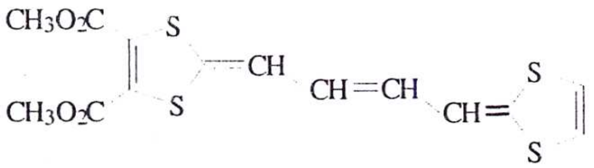
a₁



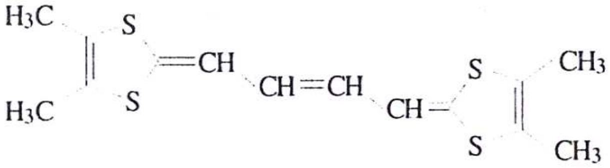
e₁



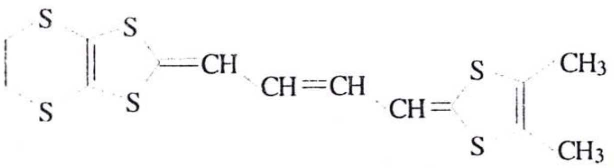
e_2



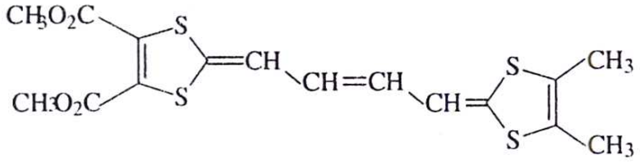
e_3



e_4



e_5



e_6

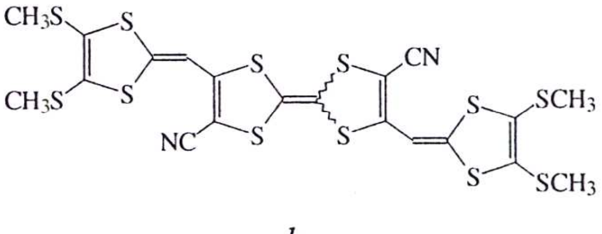
Fig. 3. The chemical structure of the acetylenic (a_1) and ethylenic ($e_1 - e_6$) derivatives

Molecules of both acetylenic and ethylenic groups present a long chain of conjugated bonds in central parts. The hyperpolarizability of ethylenic derivatives is however greater than that of acetylenic derivatives.

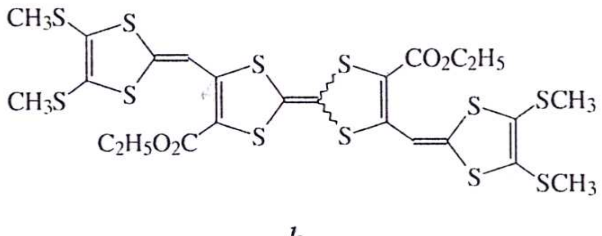
Table 1. Parameters of acetylenic (a_1) and ethylenic TTF derivatives

compound	α [cm^{-1}]	$\chi^{<3>}_{xxxx}\cdot 10^{20}$ [m^{2}V^{-2}]	$\chi^{<3>}_{xxxx}/\alpha\cdot 10^{23}$ [m^{3}V^{-2}]	$\gamma^{el}_{xxxx}\cdot 10^{45}$ [m^{5}V^{-2}]
a_1	12	2.8	2.3	1.1
e_1	13.1	2.1	1.6	4.5
e_2	9.4	3.2	3.4	5.4
e_3	26.7	7.4	2.7	3.3
e_4	21.4	8.0	3.7	1.9
e_5	8.3	1.4	1.6	1.8
e_6	14.5	8.4	5.8	7.6

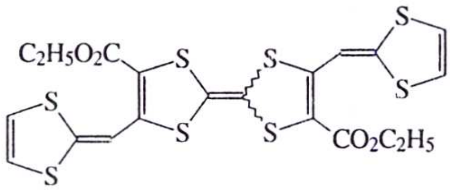
The ethylenic derivatives posses a double bond in the central part of the chain instead of a triple one in the case of acetylenic derivatives. The double bond is longer than the triple one and thus privileges the polarization of the molecule. For acetylenic and ethylenic derivatives the biggest values of γ^{el} were, respectively, 2.4×10^3 and 1.6×10^4 times greater than γ^{el} of CS_2.



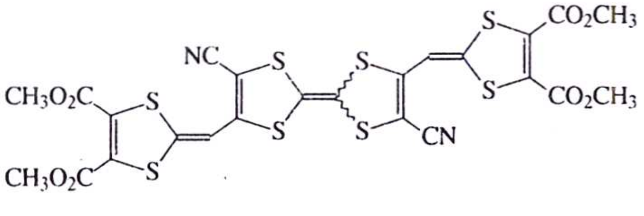
b_1



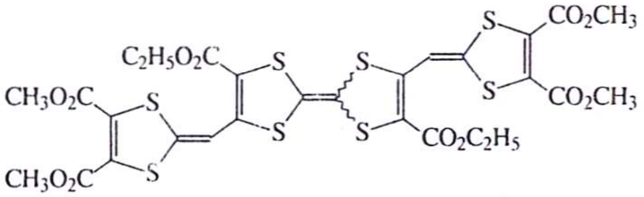
b_2



*b*₃



*b*₄



*b*₅

Fig. 4. The chemical structure of the bis-dithiafulvenyl-substituted TTF derivatives

Table 2. Parameters of bisdithiafulvenyl-substituted TTF derivatives

compound	α [cm^{-1}]	$\chi^{<3>}_{xxxx} \cdot 10^{20}$ [m^2V^{-2}]	$\chi^{<3>}_{xxxx}/\alpha \cdot 10^{23}$ [m^3V^{-2}]	$\gamma^{el}_{xxxx} \cdot 10^{45}$ [m^5V^{-2}]
b_1	19.8	3.0	1.5	113
b_2	8.6	5.2	6.0	90
b_3	1.9	1.1	5.8	29
b_4	8.2	6.4	7.8	69
b_5	20.4	14.1	6.9	65

Two important properties characterize bis-dithiafulvenyl-substituted TTF derivatives family from the point of view of a possible nonlinear optical response. First, an extended system π due to a grafting of two lateral dithiafulvenyl groups onto the skeleton of TTF. Second, the coexistence of electron-donor groups (1,3-dithiolidene) and the electron-attractor substituents (carboethoxy or nitrile) through the TTF. The important values of $\chi^{<3>}$and γ were found; the biggest value of γ^{el} is 2.4×10^5 greater than that of CS_2.

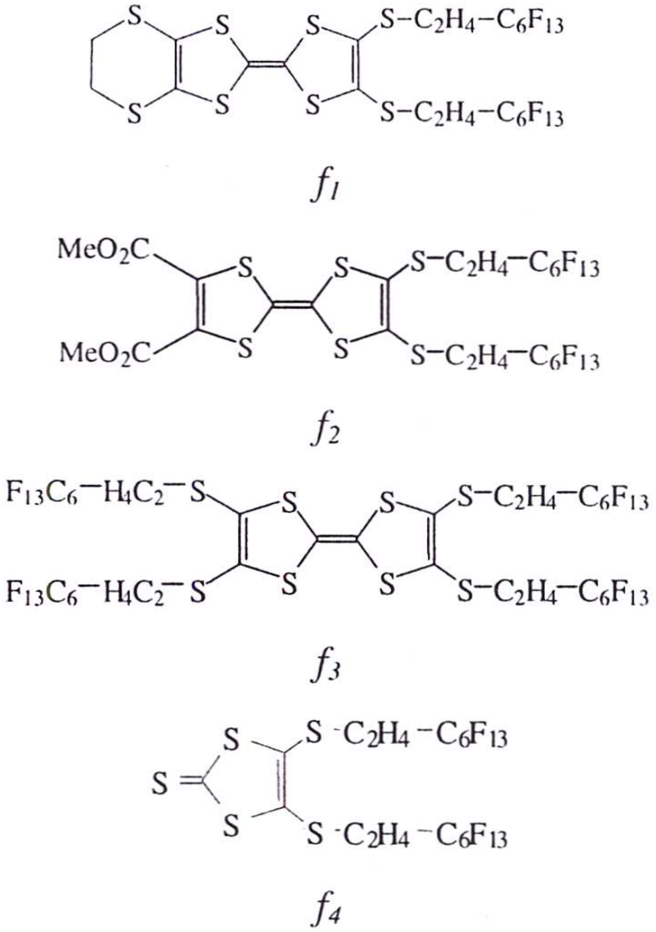
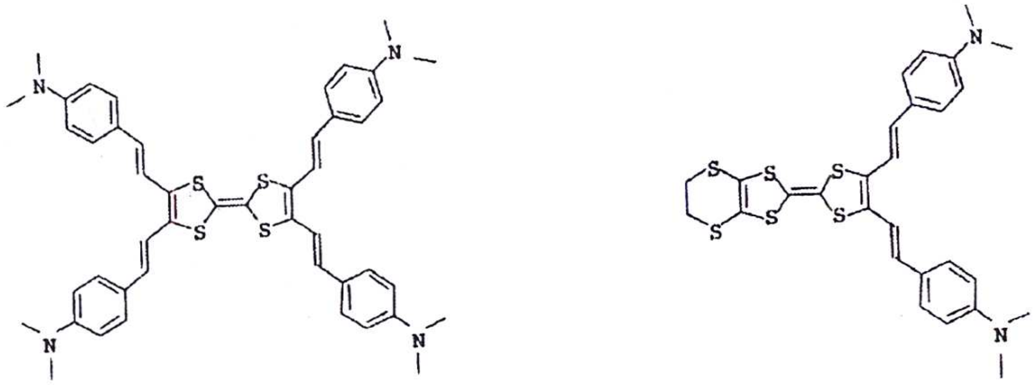


Fig. 5. The chemical structure of the polyluoroalkylosulfanyl-substituted TTF derivatives

The second order hyperpolarizabilities of the polyluoroalkylosulfanyl-substituted TTF derivatives molecules are about 10^3 than that of CS_2. One notes that these derivatives present very low absorption at 532 nm and thus an important merit factor. Table 3. Parameters of polyluoroalkylo-sulfanyl-substituted TTF derivatives.

Table 3. Parameters of polyluoroalkylo-sulfanyl-substituted TTF derivatives

compounds	α [cm^{-1}]	$\chi^{<3>}_{xxxx}\cdot10^{20}$ [m^{2}V^{-2}]	$\chi^{<3>}_{xxxx}/\alpha\cdot10^{23}$ [m^{3}V^{-2}]	$\gamma^{el}_{xxxx}\cdot10^{45}$ [m^{5}V^{-2}]
f₁	0.8	1.1	13.2	1.4
f₂	2.0	1.5	7.5	0.9
f₃	3.1	1.8	5.8	1.3
f₄	1.5	1.0	6.4	0.4



(a) (b)

Fig. 6. The chemical structure of the p-N,N'-dimethylaniline TTF derivatives

Table 4. Parameters of p-N,N'-dimethylaniline TTF derivatives

compounds	α $[\mathrm{cm}^{-1}]$	$\chi^{<3>}_{xxxx} \cdot 10^{20}$ $[\mathrm{m}^2\mathrm{V}^{-2}]$	$\chi^{<3>}_{xxxx}/\alpha \cdot 10^{23}$ $[\mathrm{m}^3\mathrm{V}^{-2}]$	$\gamma^{el}_{xxxx} \cdot 10^{45}$ $[\mathrm{m}^5\mathrm{V}^{-2}]$
a	20.6	11.4	5.5	85.2
b	16.8	9.5	5.6	27.5

The structure of these molecules presents a planar form which can promote the occurence of a fully delocalized π system over the extended framework of the molecule. In consequence, they possess large third-order nonlinear properties; the values of their second-order hyperpolarizability is about 10^5 greater than that of CS_2.

Some common properties were observed for all molecules. The values of $\chi^{<3>}$ appear to be negative. This conclusion was also confirmed by an independent test showing the defocalisation of the light beam by the studied solutions (cf.[24]). The electronic contribution to the third-order susceptibility is also negative and dominant: its absolute value is approximately one order of magnitude greater than that of a nuclear component (which is positive).

One has to note that a sixth group of TTF derivatives was also studied: the so-called hyper-TTF derivatives [25]. However, these compounds present a saturable absorption which is beyond the subject of this presentation.

Conclusions

We have reviewed recent studies of third-order nonlinear optical properties of five families of new tetrathiafulvalene derivatives. The molecular structure of these compounds suggest that they can be effectively polarized due to the presence of a long system of conjugated bonds and a number of heterocyclic rings. Such extended systems promote the occurence of fully delocalized π electrons over the extended framwork. In consequence, strong nonlinear response of the molecule to the external electric (light) field can be expected. One found large values of the third-order nonlinear susceptibility and of the second-order molecular hyperpolarizability of these materials in the region of small absorption. The values of hyperpolarizability are much larger than that of CS_2 (up to 10^5 times greater). The increase of the number of heterocycles and of dimensionality of the molecules is in favor of an increase of its hyperpolarizability. The contributions to nonlinearities due to different physical mechanisms were also estimated.

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Second Order Hyperpolarisabilities of Various Series of Organic Compounds: Tetrathiafulvalene Derivatives

Summary

We measure the third-order susceptibilities $\chi_{ijkl}^{<3>}$ of a few series of tetratiafulvalene derivatives using the degenerate four wave mixing method. From these measurements we deduce the values of the second-order hyperpolarisabilities γ and their cor-

responding molecular and electronic contributions. We compare the third-order optical properties of these new extended tetrathiafulvalene derivatives with the properties of other analogues of TTF, we have studied previously. All organic molecules studied in present work reveal large second-order non-linear optical hyperpolarisability.