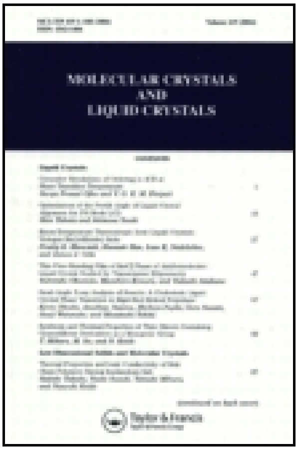

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Second Order Hyperpolarisabilities of Various Series of Organic Compounds: Tetrathiafulvalene Derivatives

B. Sahraoui [a] , X. Nguyen Phu [a] , M. Sallé [b] , J. Cousseau [b] & A. Gorgues [b]

[a] Laboratoire POMA, EP CNRS 130 Université d'Angers, 2, Boulevard Lavoisier, 49045, Angers, France

[b] Laboratoire d'Ingénierie Moléculaire Matériaux Organiques, UMR CNRS 6501 Université d'Angers, 2, Boulevard Lavoisier, 49045, Angers, France

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

B. SAHRAOUI[a], X. NGUYEN PHU[a], M. SALLÉ[b], J. COUSSEAU[b] and A. GORGUES[b]

[a]Laboratoire POMA, EP CNRS 130 Université d'Angers, 2, Boulevard Lavoisier, 49045 Angers, France and [b]Laboratoire d'Ingénierie Moléculaire Matériaux Organiques, UMR CNRS 6501 Université d'Angers, 2, Boulevard Lavoisier, 49045 Angers, France

We have measured the third-order susceptibilities $\chi^{(3)}_{ijkl}$ of a few series of tetratiafulvalene derivatives using the degenerate four wave mixing method. From these measurements we have deduced the values of the second-order hyperpolarisabilities γ and their corresponding 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.

Keywords: third-order optical susceptibilities; organic materials

INTRODUCTION

The application of nonlinear optical devices in telecommunication requires novel materials with optimised nonlinear susceptibilities. Although organic materials have great potential for use in third order nonlinear optical devices, there are currently no candidates that have sufficiently high nonlinearities and fulfill requirements such as transparency and stability. However in the recent years, there has been considerable progress in designing and characterising of molecular organic systems with high second and third order optical nonlinearities[1,2].

The present study is a natural continuation of our previous work concerning the analysis of nonlinear optical properties of a few families of tetrathiafulvalenes TTF derivatives: ethylenic, polyfluoroalkylsulfanyl-substituted, bis-dithiafulvenyl-substituted derivatives[3-5]. The obtained results are compared with those of new N,N'-dimethylaniline tetratiafulvalene derivatives. The methodology of the present study as well as the experimental technique are similar to those used in the previous work[3-5].

Technique of measurement: degenerate four waves mixing

The samples are prepared in the form of solutions of the molecules dissolved in chloroform, the thickness of the cell containing the sample is $\ell = 1$ mm. We use degenerate four wave mixing method (DFWM) to measure the third-order susceptibilities of examined organic compounds. The geometry of the experimental arrangement can be found in ref. [4-5]. The excitation is provided by 30 ps laser pulses at $\lambda = 532$ nm generated by an amplified mode locked Quantel Nd: YAG laser operating at 1 Hz repetition rate. Two of the waves are strong counterpropagating pumps travelling in the forward and backward directions. Their intensities verify the relation $I_1(z=0) = I_2(z=\ell)$. The third input wave is a weak probe (I_3, $I_4 << I_1$) which makes an angle 12° with respect to the pump wave. To interpret our experimental results we used a model based on the Maxwell nonlinear propagation equations. Using slowly varying envelope approximation and taking into account linear absorption of the medium[6]. $\chi^{(3)}$ is a real quantity due to the fact that our compounds present only linear absorption. The values of $\chi^{(3)}$ can be obtained by adjusting the mentioned theoretical model to the measured values of R. All studied compounds show the same behavior. Figure 1 shows as an example of DFWM efficiency. All studied compounds show a good agreement between experimental results of R and the theoretical model.

Two essential local effects contribute to the nonlinearities in isotropic materials submitted to such laser pulses: electronic cloud deformations and nuclear reorientation. In consequence, one can consider $\chi^{(3)}$ as being composed of two contributions corresponding to these mechanisms:

$$\chi^{(3)}_{ijkl} = \chi^{(3)el}_{ijkl} + \chi^{(3)nu}_{ijkl} \qquad (1)$$

One can show[7] that in isotropic solutions the electronic and nuclear contributions of tensorial components satisfy the following the relations:

$$\chi^{(3)el}_{xxxx} = 3\chi^{(3)el}_{xxyy} = 3\chi^{(3)el}_{yxyx} = 3\chi^{(3)el}_{yxxy} \;;\qquad \chi^{(3)nu}_{xxxx} = 8\chi^{(3)nu}_{xxyy} = 8\chi^{(3)nu}_{yxyx} = \frac{4}{3}\chi^{(3)nu}_{yxxy} \qquad (2)$$

Using the relation between the different $\chi^{(3)}$ components obtained experimentally by appropriate polarisation of incident of waves <1>, <2> and <3> we can deduce the electronic and nuclear contributions to $\chi^{(3)}$. To characterize individual molecule we have determine the second order hyperpolarisability using the following relation[8,9]:

$$\chi^{(3)} = F^4 N\,\gamma_{solution} + \chi^{(3)}_{solvent} \qquad (3)$$

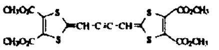
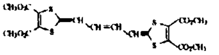
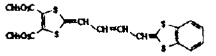
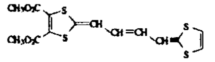
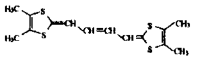
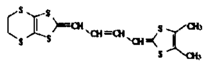
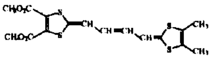
where $F = (n^2 + 2)/3$ is the Lorentz field factor correction, $N = N_A \cdot C/M$ is number of solution molecules per the unity of volume; N_A is the Avogadro number. In our case, $\chi^{(3)}_{solvent}$ can be neglected because it is small compared with $\chi^{(3)}_{solution}$ at the concentration used, which is equal to $0.126\ 10^{-20}\ V^2\ m^{-2}$.

Ethylenic TTF derivatives

The components of the third order susceptibility are deduced from the measurement of DFWM efficiency and they verify the first relationship in (4). However the relationships (2), allow us to separate molecular and electronic contributions:

$$\chi^{exp}_{xxxx} \approx 2\chi^{exp}_{xyxy} \approx 2\chi^{exp}_{xxyy} \approx 10\chi^{exp}_{xyyx} \;\Rightarrow\; \chi^{el}_{xxxx} = 1.64\chi^{exp}_{xxxx},\ \chi^{nu}_{xxxx} = -0.64\chi^{exp}_{xxxx} \qquad (4)$$

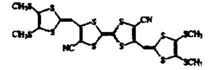
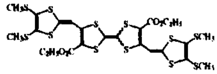
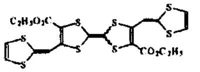
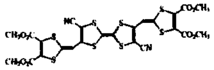
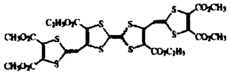
Electronic contributions, for all ethylenic analogues studied, are greater than molecular contributions and they are negative since the molecular contribution is always positive. This has been confirmed by a complementary experience concerning the self-focusing effect. This experience has shown that all solutions studied defocalised the incident beam which confirmed that $\chi^{(3)}$ is negative. The values of third order nonlinear optical parameters for ethylenic TTF derivatives are collected in the table below and in which: α, $\chi^{(3)}_{xxxx}/\alpha$ and γ^{el}_{xxxx} represent respectively the linear absorption coefficient, the measured value of the third order susceptibility, merit factor and the value of the electronic contribution of second order hyperpolarisability.

	Molecules studied	α [cm^{-1}]	$\chi^{(3)}_{xxxx}/\alpha$ $\cdot 10^{23}$ [m^{3}V^{-2}]	$\gamma^{el}_{xxxx}\cdot 10^{45}$ [m^{5}V^{-2}]
a_1		12	2.3	-1.12
e_1		13.1	1.6	-4.54
e_2		9.4	3.4	-5.47
e_3		26.7	2.7	-3.32
e_4		21.4	3.7	-1.88
e_5		8.3	1.6	-1.82
e_6		14.5	5.8	-7.58

The second order hyperpolarisability of ethylenic TTF derivatives is greater that γ^{el} of acetylenic TTF derivatives so we can conclude that the insertion of double bond in the path of the conjugation increases γ. The compound e_6 in which the end groups are methoxy-carbonyl (electron-withdrawing group) and methyl (electron-donating substitution) posses the largest γ and the largest merit factor.

Bis-dithiafulvenyl substituted TTF derivatives

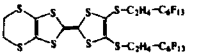
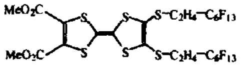
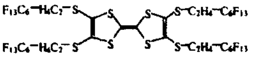
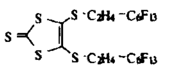
The experimental DFWM efficiency for bis-dithiafulvenyl substituted TTF derivatives are similar to those shown in Fig. 1. From DFWM measurements on bis-dithiafulvenyl substituted TTF derivatives and taking into account eq. (2) and (3) we deduced the electronic and molecular contributions in $\chi^{(3)}_{xxxx}$ as we did in the case of ethylenic TTF derivative. The obtained results are collected in the below table:

	Molecules studied	α [cm^{-1}]	$\chi^{(3)}_{xxxx}/\alpha \cdot 10^{23}$ [m^{3}V^{-2}]	$\gamma^{el}_{xxxx} \cdot 10^{45}$ [m^{5}V^{-2}]
b_1		19.8	1.5	-113
b_2		8.6	6.0	-90
b_3		1.9	5.8	-29
b_4		8.2	7.8	-69
b_5		20.4	6.9	-65

We have found that the electronic part of γ for the compound b_1 is $2.4 \cdot 10^5$ time greater than for CS_2 and 15 time greater than for e_6. The merit factor $\chi^{(3)}_{xxxx}/\alpha$ for the molecules $b_2 - b_5$ is better than in the ethylenic derivatives. This result suggests that the increase of the number of sulfur heterocycles in a molecule plays a major role in the obtaining the important values of third order nonlinearities.

Polyfluroalkysulfanyl-substituted TTF derivatives

The chemical structures of polyfluroalkysulfanyl-substituted TTF derivatives and their optical parameters are presented in the below table, the different components of $\chi^{(3)}$ and γ are deduced from the experimental results of DFWM efficiency:

	Molecules studied	α [cm^{-1}]	$\chi^{exp}_{xxxx} \times 10^{20}$ [m^{2}V^{-2}]	$\chi^{(3)}_{xxxx}/\alpha$ $\cdot 10^{23}$ [m^{3}V^{-2}]	$\gamma \cdot 10^{46}$ [m^{5}V^{-2}]
f_1		0.83	1.1	13.2	9.5
f_2		1.98	1.5	7.5	6.0
f_3		3.1	1.8	5.8	9.7
f_4		1.5	0.96	6.4	2.3

We have found that the molecules under consideration posses small absorption so their merit factor is relatively large compared to acetylenic analogues of TTF and to the ethylenic TTF derivatives studied previously. The second order hyperpolarisabilities of the studied molecules are about 10^3 times greater than γ of CS_2, which is the reference material for DFWM measurements.

p-N,N'-dimethylaniline TTF derivatives

The p-N,N'-dimethylaniline TTF derivatives have been designed in order to allow planarity of their molecular structure, and therefore to promote occurrence of fully delocalized π-system over the extended framework, which make them suitable candidates to reveal large third-order nonlinear optical susceptibilities. Figure 1 presents an example of DFWM results: R_{xxxx} versus $I^{<1>}$ in the case of vertical polarization of the incident beams for the both components studied.

Taking into account the relationship obtained from the measurement of DFWM efficiency R, and different spatial symmetries involved in the $\chi^{(3)}$ tensor and we can distinguish different physical mechanisms contributing to $\chi^{(3)}$, that is electronic and molecular part for compounds (a) and (b):

$$\text{(a)}: \chi^{el}_{xxxx} \cong 1.2\chi^{exp}_{xxxx}, \chi^{nu}_{xxxx} \cong -0.2\chi^{exp}_{xxxx} \quad \text{(b)}: \chi^{el}_{xxxx} \cong 1.53\chi^{exp}_{xxxx}, \chi^{nu}_{xxxx} \cong -0.53\chi^{exp}_{xxxx} \quad (5)$$

Hence, we can then conclude that the electronic contribution is much larger than the nuclear contribution for the both molecules of interest. For molecule *a* the electronic contribution in third order susceptibilities is larger than for molecule *b*. It can be related with the fact that *a* has more extended structure which favour the π electrons delocalisation.

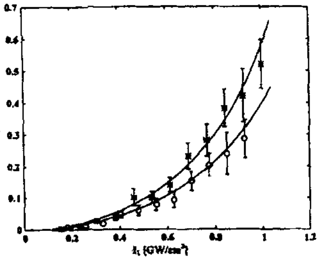
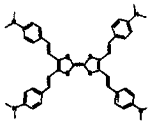
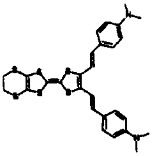


FIGURE 1. R_{xxxx} versus pump intensity for the molecule *a* (°) and, *b* (*).

	Molecules studied	α [cm^{-1}]	$\chi^{exp}_{xxxx} \times 10^{20}$ [m^{2}V^{-2}]	$\chi^{(3)}_{xxxx}/\alpha \cdot 10^{23}$ [m^{3}V^{-2}]	$\gamma \cdot 10^{45}$ [m^{5}V^{-2}]
a		20.6	11.4	5.5	71
b		16.8	9.5	5.6	18

From the table above, we can conclude that the third order susceptibility of p-N,N'-dimethylaniline TTF derivatives is larger than in ethylenic derivatives, but the merit factor is only a bit larger; the merit factors of bis-dithiafulvenyl substituted TTF derivatives $b_2 - b_5$ and polyfluroalkysulfanyl-substituted TTF derivatives are better because their absorption coefficient is smaller. The second order hyperpolarisabilities values p-N,N'-dimethylaniline TTF derivatives are important: about 10^5 times greater than γ of CS_2.

CONCLUSIONS

In conclusion, we have shown that the molecules under consideration posses large third order nonlinear optical properties compared to the polyazine derivatives, acetylenic analogues of TTF[3]. The increase of the number of the heterocycles and the dimensionnality of the molecule is in favour of an increase of γ. We found that the electronic part of third order susceptibility $\chi^{(3)}$ the molecules studied is dominant and its sign is negative. The second order hyperpolarisabilities of the studied molecules are a few order greater than γ of CS_2.

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