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Third-order nonlinear optical susceptibilities in octupolar molecules

Introduction

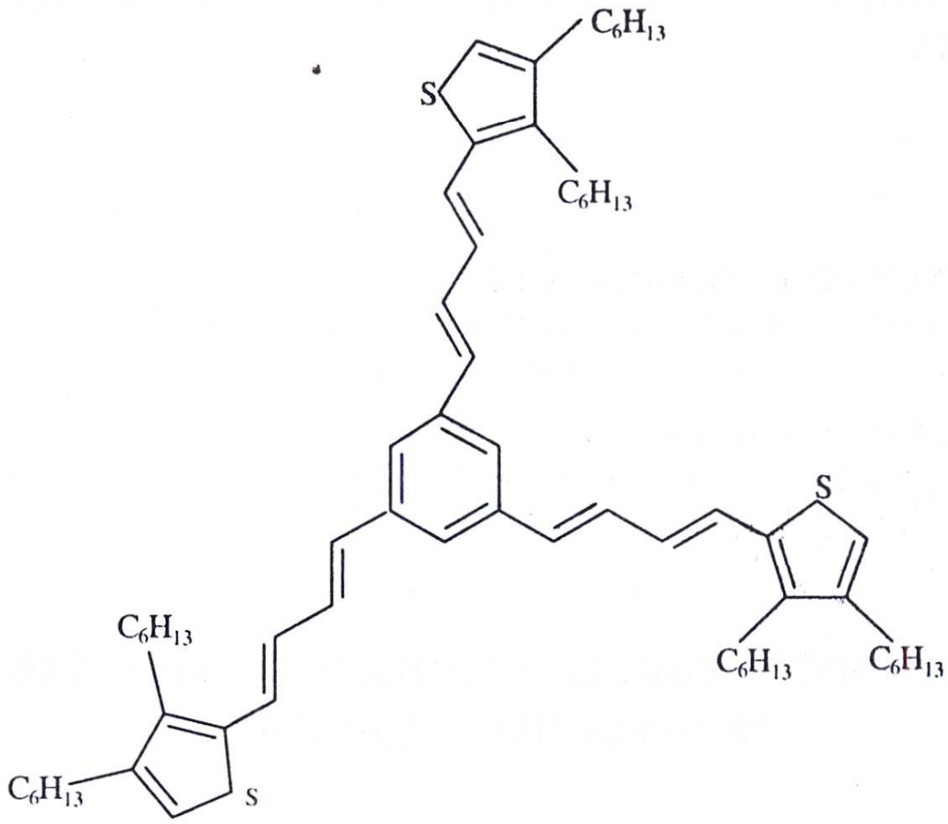
Research of organic materials that can be potentially used in fabrication of nonlinear optical devices is currently an interesting subject of investigation [1–3]. Particular interest presents the nonlinear optics have been observed in molecules with highly delocalized π electrons, in which the chain of conjugated bonds facilitates the polarization of the molecule in external electromagnetic field. The organic conjugated molecules can possess large third-order nonlinearities which are advantageous for nonlinear optical applications. Experimental and theoretical investigations have revealed that the organic materials exhibit large third order optical nonlinearities and low optical losses as well as a fast time response.

In the present paper, we report experimental investigations of the third-order nonlinear optical susceptibility $\chi^{<3>}$ of two octupolar molecule using the standard degenerate four wave mixing (DFWM) technique at $\lambda = 532$ nm.

In this paper, we report on a systematic study of the third order nonlinear optical properties of two new octupolar molecules with different numbers of π conjugated bonds.

The chemical structure of the studied compounds is shown in the Fig. 1. They were synthesized using a method that described in Ref. [4].

A



B

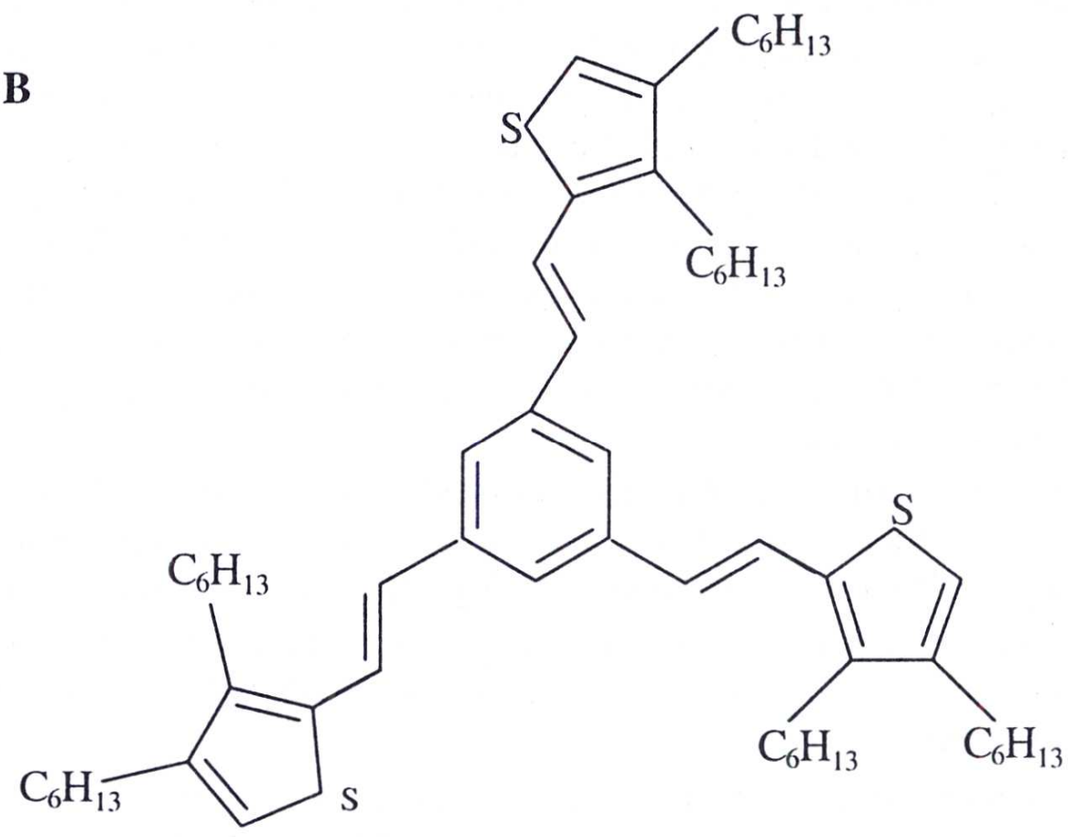


Fig. 1 A–B. The chemical structure of the octupolar molecules

Experimental method

The absolute value $\chi^{<3>}$ for $C_{66}H_{96}S_3$, $C_{60}H_{90}S_3$ was estimated using the DFWM method. The idea of The DFWM is shown in Fig. 2.

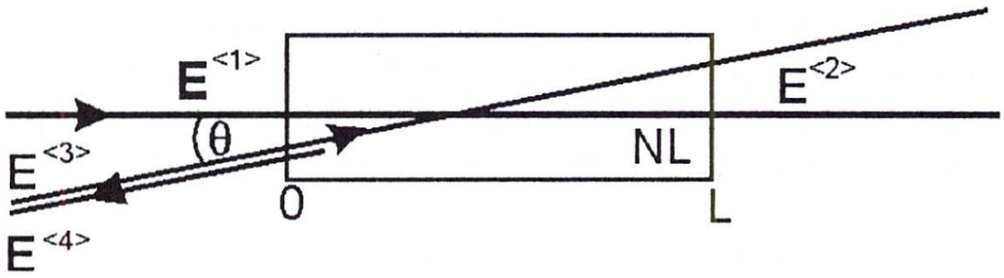


Fig. 2. Schematic diagram of the geometry to the light beams in an four wave mixing experiment

$E^{<1>}$ and $E^{<2>}$ designate the exactly counter-propagating pump waves and $E^{<3>}$ designates the probe wave, which makes a nonzero angle θ with respect to the pump wave ($E^{<1>}$). Phase matching requires that the «phase conjugate» signal wave (designated by $E^{<4>}$) is propagated in a direction opposite to the probe wave. In our setup experiment the incident wave intensities satisfy the conditions: $I_1 (z = 0) = I_2 (z = L)$ and $I_3 = 10^{-2} \cdot I_1$.

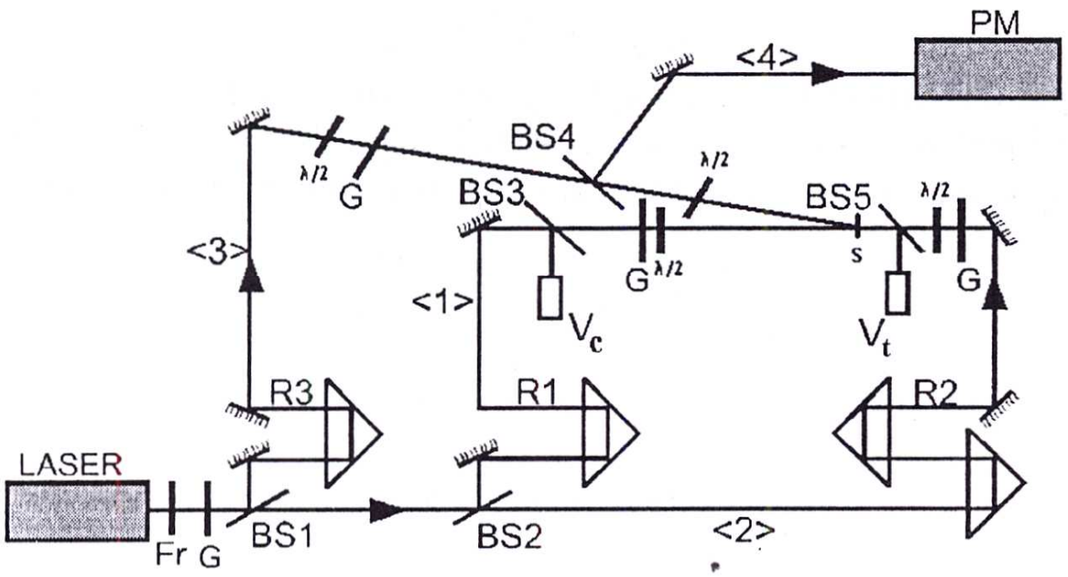


Fig. 3. Experimental setup: S — sample; F_T — neutral filter; R_1 – R_3 delay lines; G — glan prism; V_c, V_t — control photodiodes; PM — photomultiplier tube; BS — beam splitter 3

The angle θ between the beams <1> and <3> in air is 12° and the thickness of the cell containing the sample is L = 1 mm. The incident beams have linear polarization xxx [5,6]. A Q-switched mode-locked Nd :YAG laser with 30 ps pulse width, 1 Hz repetition rate and 532 nm wavelength was used.

Two main 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 (> 1 ns) thermal and electrostricted effects can be neglected. From the nonlinear intensity dependent transmission at λ = 532 nm and using the theoretical formula, we evaluated the values of the TPA coefficient (β). The nonlinear intensity dependent transmission is described by expression [7]:

$$T = \frac{I(L)}{I(0)} = \frac{\alpha \cdot \exp(-\alpha \cdot L)}{\alpha + \beta I(0) \cdot (1 - \exp(-\alpha \cdot L))} \tag{1}$$

where L is the thickness of the sample, β is the non-linear absorption coefficient, α is the linear absorption coefficient.

The important characteristic of the DFWM process is its efficiency defined as:

$$R = \frac{I^{<4>}(z=0)}{I^{<3>}(z=0)} \tag{2}$$

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. The laser waves propagating in the medium are taken as plane waves:

$$E^{<1>}(r,t) = E^{<i>} e^{i(k_i r - \omega_i t)} \tag{3}$$

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:

$$\begin{cases} \dfrac{\partial E_1}{\partial z} = -\dfrac{\alpha}{2} E_1 + iH\chi^{<3>} \cdot (E_1 E_1^* + 2E_2 E_2^*) E_1 \\ \dfrac{\partial E_2}{\partial z} = \dfrac{\alpha}{2} E_2 - iH\chi^{<3>} \cdot (2E_1 E_1^* + E_2 E_2^*) E_2 \\ \dfrac{\partial E_3}{\partial z} = -\Phi E_3 + 2iH\chi^{<3>} \cdot E_1 E_2 E_4^* \\ \dfrac{\partial E_4}{\partial z} = \Phi E_4 - 2iH\chi^{<3>} \cdot E_1 E_2 E_3^* \end{cases} \tag{4}$$

where : $E_i = E_x^{<i>}$, $\chi_{ijkl}^{<3>} = \chi_{xxxx}^{<3>}$, $H = \dfrac{12 \cdot \pi^2}{n \cdot \lambda}$, $\Phi = \dfrac{\alpha}{2} - 2i \cdot H \cdot \chi^{<3>}(E_1 E_1^* + E_2 E_2^*)$,

n is the linear refracitve 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 : $I_i = \frac{n \cdot c}{2 \cdot \pi} \cdot E_i \cdot E_i^*$.

The DFWM efficiency (R) was calculated from the propagation equation of the four beams in interaction and took into account linear and nonlinear absorption:

$$R = \frac{I_4(0)}{I_3(0)} = \begin{cases} \dfrac{K^2}{\left[p \cdot \mathrm{ctg}(pl) - \dfrac{\Psi}{2}\right]^2} & \Psi^2 - 4 \cdot K^2 \le 0 \\ \dfrac{K^2}{\left[q \cdot \mathrm{ctgh}(ql) - \dfrac{\Psi}{2}\right]^2} & \Psi^2 - 4 \cdot K^2 > 0 \end{cases} \qquad (5)$$

where $p^2 = K^2 - (\Psi/2)^2$ and $q = i \cdot p$

The imaginary part $\chi^{<3>}$ is related to the nonlinear absorption coefficient:

$$\beta = 24 \cdot \frac{\omega \cdot \pi^2}{n^2 \cdot c^2} \cdot \chi'' \qquad (6)$$

Results and discussion

The estimated nonlinear intensity dependence transmission as a function of the incident light intensity is shown in Fig. 4.

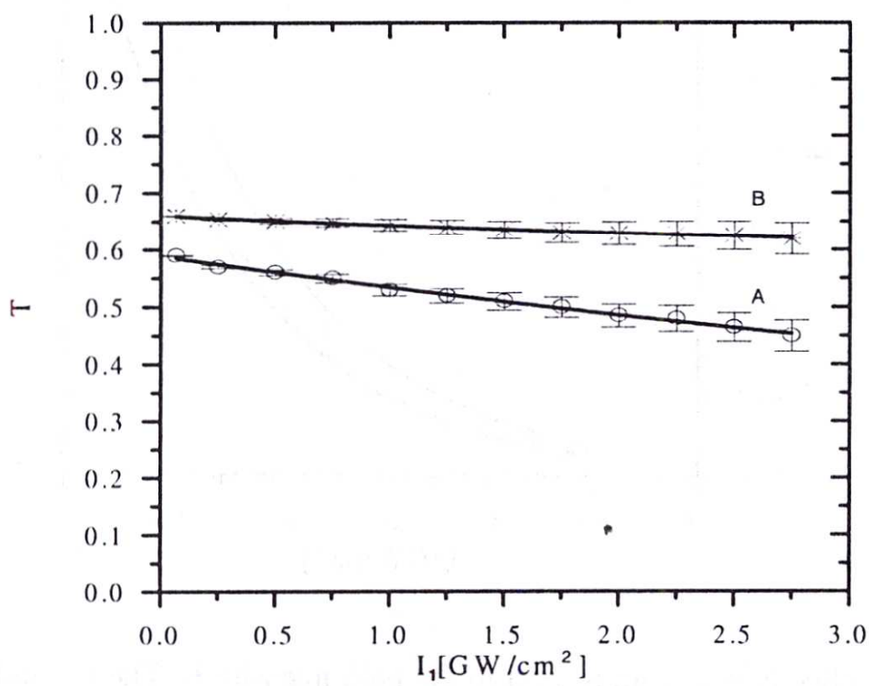


Fig. 4. The transmission T as a function of the incident beam intensity I_1. for (o) A and (✳) B

The solid line in Fig. 4. shows the best fit with Eq. (1). The values of the TPA coefficient (β) extracted from dependencies of Fig. 4. and theoretical formula (1) are presented in Table 1.

Table 1.

Molecules	α [cm^{-1}]	β [$cm\ GW^{-1}$]	$\chi^{<3>}$ [esu]	$\chi^{<3>} / \alpha$ [esu·cm]
A	5.2	1.3	2.4×10^{-12}	4.6×10^{-13}
B	4.1	0.1	1.6×10^{-12}	3.9×10^{-13}

We measured two compounds A and B [see Fig. 1] possessing different number of conjugated chemical bonds. The studied compounds were in a form of powder dissolved in the THF (2.5 g/L). For each compounds we studied the absorption and the output DFWM process. This study is made in order to determine the influence on the third order nonlinear properties versus the number of bond in the case of A and B compounds.

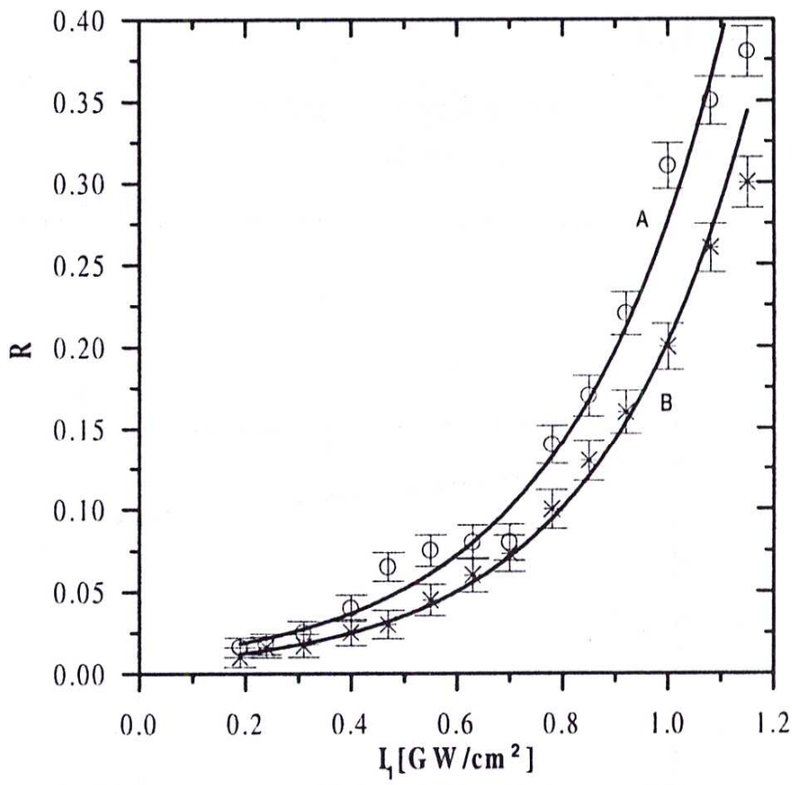


Fig. 5. DFWM reflectivity R with respect to the pulp intensity I_1. The (o) and (✳) represent experimental data, respectively, for $C_{66}H_{96}S_3$ (A), $C_{60}H_{90}S_3$ (B)

Figure 5 presents of these results: R versus $I^{<1>}$ in the case of vertical polarization of incident beams for the compounds A and B. A good agreement between experimental results and theoretical curve given by Eq. 5. is observed in these cases.

Both the compounds studied possess the nonlinear optical properties of the third order much higher with comparison to materials known for their elevated nonlinearites of the third order [8].

The value of the $\chi^{<3>}$ clearly increases with the increasing number of doubled π conjugated bonds of the molecule (from three to five). At the same time the value of β increases also. It is important fact that the figure of merit $\chi^{<3>} / \alpha$ increases also with increasing number of π-conjugated bonds that is very important for their application as optical limiting materials. The obtained values of figure of merits comparing with other materials opens a possibility of their application in optical limiters.

Conclusions

An experimental study of third-order nonlinear optical properties of octupolar organic materials has been presented. We have evaluated the third-order susceptibility $\chi^{<3>}$ for two octupolar compounds with different number of the conjugated chemical bonds. We concluded that the number of double bonds in the molecular structure favors increasing optical limitation effect as well as the nonlinear optics in general. The increase of the number of double bonds facilitates the delocalisation of the electrons, and thus allows the increase of $\chi^{<3>}$, what is in a good agreement with the known theoretical data [9]. Organic materials are good modeling subject for investigations of the third-order nonlinear optical susceptibilities, because they possess high level of the π-conjugated charge transfer. The value of the $\chi^{<3>}$ of the compound A is higher than that of the compound B and is due to the larger number of π conjugated bonds. The values of corresponding figure of merits 3.9×10^{-13} and 4.6×10^{-13} [esu · cm] allow to apply them as effective optical limiters.

References

[1] F. Kajzar, J. Messier, „J. Phys. Rev." A, V. 32, p. 2352, (1985).

[2] P.N. Prasad, D.J., *Williams, Introduction Nonlinear Optical Effects in Molecules and Polymers*, Wiley, New York (1991).

[3] J. Zyss (ED), *Molecular nonlinear optics: Materials, Physics and Devices*, Academy Press, Boston, (1994).

[4] Corinne Martineau, *Nanostructures cojuguees derivees du thiophene et du fullerene C_{60}*, Thesis N°500, Angers (2001).

[5] B. Sahraoui, G. Rivoire, M. Sylla, X.N. Phu, J. Zaremba, T.T. Nguyen, M. Salle, „Optica Applicata", V. 26, p. 341, (1996).

[6] B. Sahraoui, J. Zaremba, X.N. Phu, M. Salle, J. Cousseau, A. Gorgues, „Appl. Phys.", V. 1, p.17, (2000).

[7] B. Sahraoui, R. Chevalier, X. N. Phu, G. Rivoire, W. Bala, „J. Appl. Phys." V. 80, p. 4854, (1996).

[8] B. Derkowska, J. C. Mulatier, I. Fuks, B. Sahraoui, X.N. Phu, C. Anraud, JOSA B, V. 18, p. 610, (2001).

[9] I. Fuks, B. Derkowska, B. Sahraoui, S. Niziol, J. Sanetra, D. Bogdal, J. Pielichowski, JOSA B, V. 19, p. 89, (2002).

[10] B. Sahraoui, I. V. Kityk, I. Fuks, B. Paci, P. Baldec, J-M. Nunzi, P. Frere, J. Roncali, „J. of Chemical Physics", V. 115, P, 6179, (2001).

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Summary

We report measurements of the third-order susceptibilities and two-photon absorption in new synthesized $C_{66}H_{96}S_3$, $C_{60}H_{90}S_3$ compounds, using degenerate four wave mixing (DFWM) technique at $\lambda = 532$ nm in picosecond regime. We have found that increasing number of double bonds favors increasing $\chi^{<3>}$.

The values of figure of merit are equal to 3.9×10^{-13} [esu·cm] and $4.6 \times \times 10^{-13}$ [esu·cm], respectively. That is sufficient for their application as optical limiting materials.

Keywords: two-photon absorption; third order nonlinear optical susceptibility; organic materials.