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Quantum-Chemical Calculations of First-Order Hyperpolarizability of Epoxy Oligomers with Chromophore in the Main Chain*

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Results of quantum-chemical calculations of first hyperpolarizabilities for a number of epoxy oligomers with nonlinear optical (NLO) chromophores incorporated into the main chain as a side group are presented. These oligomers simulate the internode chains of cross-linked NLO materials, which are the most promising candidates for application in optoelectronics. The attempt is made to establish a relationship between the hyperpolarizability and the conformation of the bearing chain in the vicinity of the chromophore. The structure and conformation of the oligomer chain are shown to affect significantly the longitudinal hyperpolarizability of the chromophore. Some recommendations are given to obtain hyperpolarizability values optimal for the studied molecular systems.

Key words: hyperpolarizability, NLO chromophores, epoxy oligomers, quantum-chemical calculations

New organic materials, exhibiting nonlinear optical (NLO) response to high-intensity laser field, may be constructed on the basis of cross-linked polymer electrets – materials, which preserve constant nonzero polarization in the absence of applied electric field [1]. Such materials are prominent candidates for use in photonics and optoelectronics. For instance, the 2nd order materials are needed for high-speed waveguide devices, controlling light signals in fiber-optical communication lines [2,3]. Polymer electrets are unique, as their NLO properties may be selectively optimized using almost unlimited potentialities of fine organic synthesis and macromolecular chemistry. Elaboration of design strategy for construction of electret structures with required properties is a burning problem, which should be solved both at the molecular and supramolecular level, and needs combined and consistent efforts of theoretists and experimentalists.

Macroscopic NLO response of the material originates at the microscopic level mainly from the NLO response of the constituent groups, possessing constant dipole moment and hyperpolarizability, the so-called NLO chromophores. At present di-

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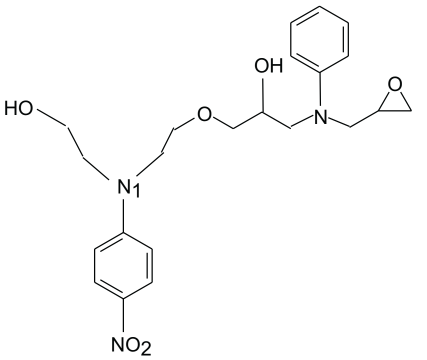
polar molecules with extended π-electron bridge, connecting π-donor and π-acceptor groups, are used as NLO chromophores. The system of π-conjugated bonds provides a fast and large NLO response of the chromophore. The available theoretical models and experimental data enabled the selection of molecular structures which are promising NLO chromophores [4]. This task has been fulfilled mainly due to the computational quantum-chemical techniques, which, on the one hand, allow to determine the mechanism of NLO response formation, and, on the other hand, to study the dependence of molecular hyperpolarizability on donor and acceptor strength of the end groups, as well as on the length and nature of conjugated π-electron bridge [5].

Quadratic susceptibility of electret depends not only on the characteristics of the individual NLO unit, but also on the concentration of chromophores in a polymer matrix, on the degree of their orientation along the direction of the applied electric field, and on the effect of local electric fields created at the chromophores by their environment in a polymer matrix [6]. In the course of the electret construction it is necessary to provide the greatest possible value and relaxational stability of NLO response of the material [7]. The polymer cross-linking after poling seems to be the most reasonable strategy to satisfy this requirement. The conventional process of orientation of dipolar chromophores in a polymer matrix by the applied electric field results in the deformation of bearing chains and in the changes of conformational state of NLO chromophores. That is why of prime importance is the establishing at the micro-level of the relationship between chromophore hyperpolarizability and the conformation of bearing chain in the vicinity of the chromophore. Up to now this problem has not been understood, though it is one of the most crucial for the optimization of the synthesis strategies of nonlinear optical polymer electrets.

This work presents one of the first steps in this direction. We focus on the materials with chromophores incorporated into the main chain of the polymer other than on traditionally studied composite materials, where chromophores are present as guest molecules. Here, we have chosen the oligomers of finite length, containing chromophore group as a side group of the main chain, to simulate an internode chain of a cross-linked NLO matrix, and we have made an attempt, staying at the molecular level, to study the effect of structure and conformation of polymer chain on the hyperpolarizability of this molecular unit. We have chosen *p*-nitroaniline as a chromophore; its hyperpolarizability is not large, but it permits to examine the effect of polymer matrix on the chromophore with aromatic rings as π-electron bridge. Oligomers of epoxy polymers serve as a backbone chain. The studied molecules are the following: oligomers based on diglycidyl aniline – **I** (n = 1, where n is the number of epoxy fragments) and **II** (n = 2), and oligomer based on diglycidyl ether of diphenylol propane **III** (n = 1); they are presented in Fig. 1. Epoxy oligomers are chosen for this study as they are the most appropriate for the construction of thick networks, fixing orientation of chromophores within the electret. Besides, keeping in mind the next stage of electret construction – the orientation of chromophore groups by the electric field – chromophore group is attached to the polymer chain by flexible ethoxy tails, providing the mobility of chromophores in the orienting field.



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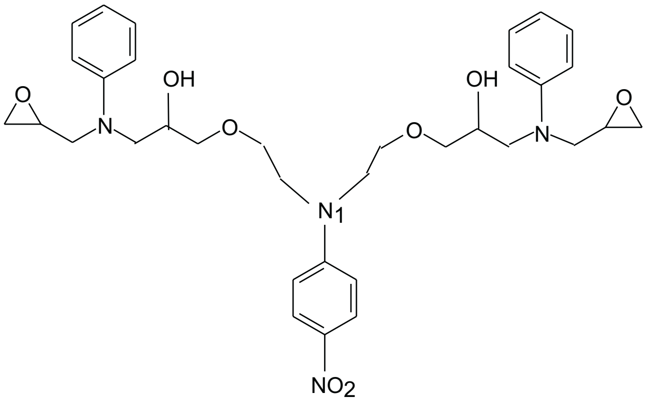

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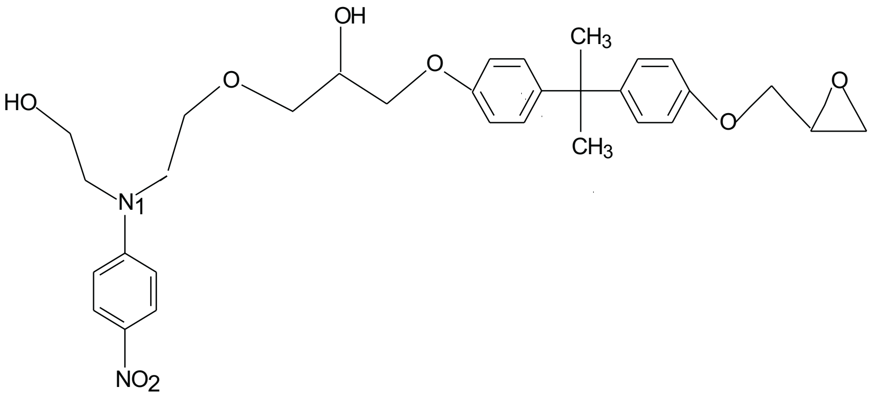


III

Figure 1. Structures of the molecules studied in this work: oligomers based on diglycidyl aniline – **I** (n = 1, where n is the number of epoxy fragments) and **II** (n = 2), and oligomer based on diglycidyl ether of diphenylol propane **III** (n = 1).

EXPERIMENTAL

The dipole moment of a molecule interacting with an external electric field

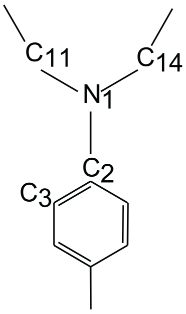
$$\mu_i = \mu_{0i} + \alpha_{ij}\cdot E_j + 1/2\beta_{ijk}\cdot E_j E_k + 1/6\gamma_{ijkl}\cdot E_j E_k E_l + \dots \qquad (1)$$

defines the components of the α, β, γ tensors, which correspond to the first-, second-, and third-order polarizabilities (β, γ are also called hyperpolarizabilities of the 1st and 2nd orders, correspondingly); μ_{0i} – is a permanent dipole moment of a molecule. Thus, α, β, γ may be estimated as partial derivatives of the first, second and third order of the induced dipole moment with respect to the electric field components.

Structural parameters of the studied systems were obtained as a result of optimization by semi-empirical AM1 technique [8]. Calculation of longitudinal hyperpolarizability β_{xxx} was carried out by Time Dependent Hartree-Fock (TDHF) technique [9] with the wave function of AM1 method as implemented in the GAMESS program package [10]. Here, we analyze β_{xxx}, as the **x** axis coincides with the longitudinal axis of the chromophore, and this component of hyperpolarizability tensor is the largest one.

RESULTS AND DISCUSSION

Let us consider first of all the chromophore fragment, that is the chromophore group with two ethoxy groups at nitrogen. From general considerations, confirmed by the calculations of β_{xxx}, the structure with planar aniline fragment provides the greatest possible value of hyperpolarizability. That is why we have used the value of β_{xxx} for this structure with planar chromophore group – **A** – as a reference one. We have studied then the effect of two structural factors on β_{xxx}: the rotation of aromatic ring around the N_1–C_2 bond, $\alpha = C_{11}N_1C_2C_3$ being the corresponding angle, and the deviation of configuration of nitrogen bonds from planarity, $\varphi = C_{11}N_1C_2C_{14}$ being the corresponding angle.



The corresponding conformations are denoted as **A**α and **A**φ, pointing explicitly to the structural parameter being optimized. It is seen from Table 1, that the structure with planar chromophore group, **A**, is in fact preferable: the rotation of the ring does not affect the value of β_{xxx}, and the deviation from planarity, as might be expected, slightly lowers hyperpolarizability. It can be concluded, that while choosing the reactive groups, through which chromophore is attached to the polymer chain, it is worth using those, which favor the planar configuration of nitrogen bonds, providing optimal β_{xxx}. Chromophore fragments with one or two phenoxy groups may be considered for this purpose.

Table 1. Effect of geometrical parameters of chromophore fragment on longitudinal hyperpolarizability*).

	A	**A**α	**A**φ
ΔE (kcal/mole)**)	1.0	0.0	0.8
α (°)	0.0	18.6	0.0
φ (°)	180.0	180.0	143.0
μ (**D**)**)	7.8	7.5	5.6
$\beta_{xxx} \cdot 10^{-30}$ (esu)***)	21.2	21.5	17.8

*) Chromophore fragment consists of the chromophore group and two ethoxy groups binding it to oligomer chain. The idealized planar structure is used for the chromophore group (conformation **A**), for **A**α and **A**φ conformations only α and φ correspondingly were optimized, other structural parameters being fixed (see the text for notations).

**) ΔE (kcal/mole) – relative values of the total energy of different conformations; $\mu(D)$ – the value of the dipole moment.

***) β_{xxx} is presented in electrostatic units here; $\beta(\text{esu}) = \beta(\text{au}) \cdot 0.86392 \cdot 10^{-32}$.

When studying the polymer chain effect on the chromophore hyperpolarizability, the following structures were examined: the structures with nearly transoidal bonds in the epoxy fragment (denoted as **T** in Table 2) and the structures with convoluted chains with minimal distances between the chain ends (**C** in Table 2). The corresponding model structures for oligomer **III** are shown in Fig. 2. The chromophore fragment structure was fixed.

The data presented in Table 2 for oligomer **III** demonstrate that conformation **T** is the most preferable one, *i.e.* having the highest hyperpolarizability, the β_{xxx} value for **C** is significantly lower, demonstrating the reduction of β_{xxx} due to the interaction through space.

The conformation of the remote chain segments does not essentially affect the chromophore fragment planarity, the deviation from planarity is controlled mostly by the conformations of ethoxy groups at nitrogen. This confirms the above made conclusion about the importance of choice of optimal linking groups at nitrogen. It is seen from Table 2 for oligomer **III**, that both the ring rotation (by 6.1° – **T**α, by 2.4° – **C**α) and the deviation of nitrogen bonds from the planar configuration (the angle φ being equal to 174.9° – **T**φ, –178.2° – **C**φ) almost do not affect β_{xxx} for the given conformation. The validity of conclusions made above was tested by the examination of oligomer **I**, the results of the corresponding calculations are summarized in Table 2. The comparison of the results for oligomers **I** and **III** illustrates the effect of backbone chain length. The chain of oligomer **I** is substantially shorter, what results in vanishing the difference in β_{xxx} for **T** and **C** conformations. The distance between the chain ends for **T** conformers (**R** in Table 2; **R** is defined here as the distance between the end

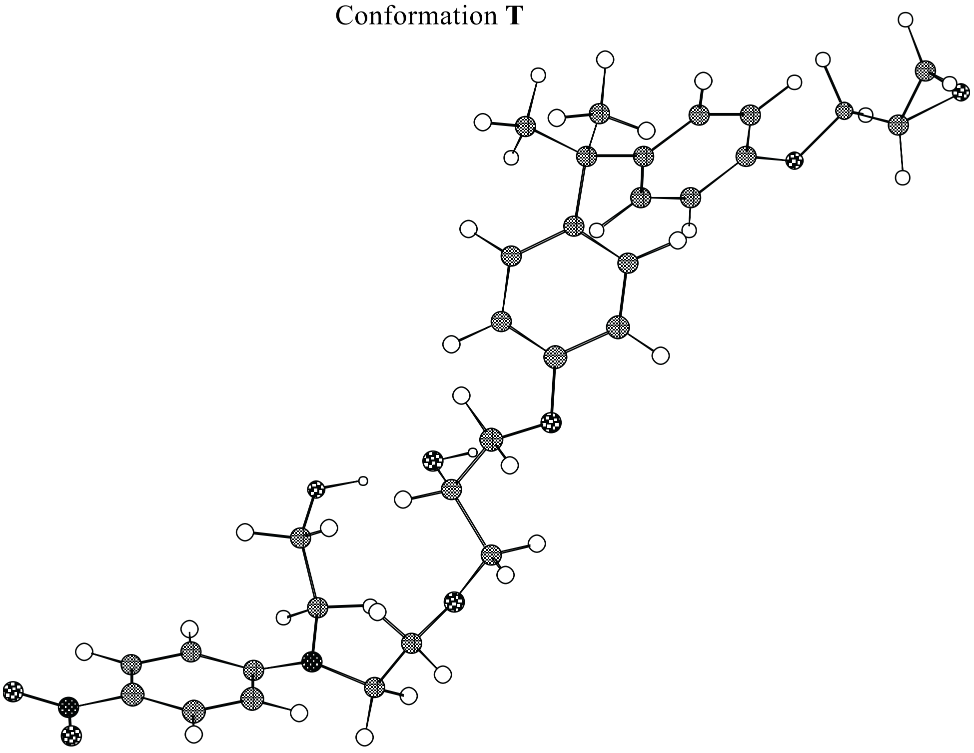
Table 2. Effect of the epoxy fragment conformation and the structural characteristics of chromophore fragment on hyperpolarizability of oligomers **I** and **III** (model calculation)*⁾.

Conformation	Oligomer **I**						Oligomer **III**					
	T	**T**α	**T**φ	**C**	**C**α	**C**φ	**T**	**T**α	**T**φ	**C**	**C**α	**C**φ
α (°)	0.0	12.5	0.0	0.0	26.0	0.0	0.0	6.1	0.0	0.0	2.4	0.0
φ (°)	180.0	180.0	174.3	180.0	180.0	160.0	180.0	180.0	174.9	180.0	180.0	–178.2
R (**A**)**⁾	14.1	14.1	14.1	9.8	9.2	9.2	24.6	24.6	24.6	3.8	3.8	3.8
μ (**D**)**⁾	7.1	8.1	8.1	9.0	8.8	8.9	9.1	9.3	8.9	6.4	6.4	6.4
$\beta_{xxx}\cdot 10^{-30}$ (esu)	24.1	24.0	24.0	23.6	23.3	22.6	27.1	27.0	27.0	20.6	20.6	20.6

*⁾ For **T** and **C** conformations the idealized planar structure is used for the chromophore group, for **T**α, **C**α and **T**φ, **C**φ conformations only α and φ correspondingly were optimized, other structural parameters being fixed (see the text for notations).

⁾ **R (**A**) – the distance between the chain ends: the end group of epoxy fragment and NO_2 group of the chromophore; μ (**D**) – dipole moment.

Conformation **T**



Conformation **C**

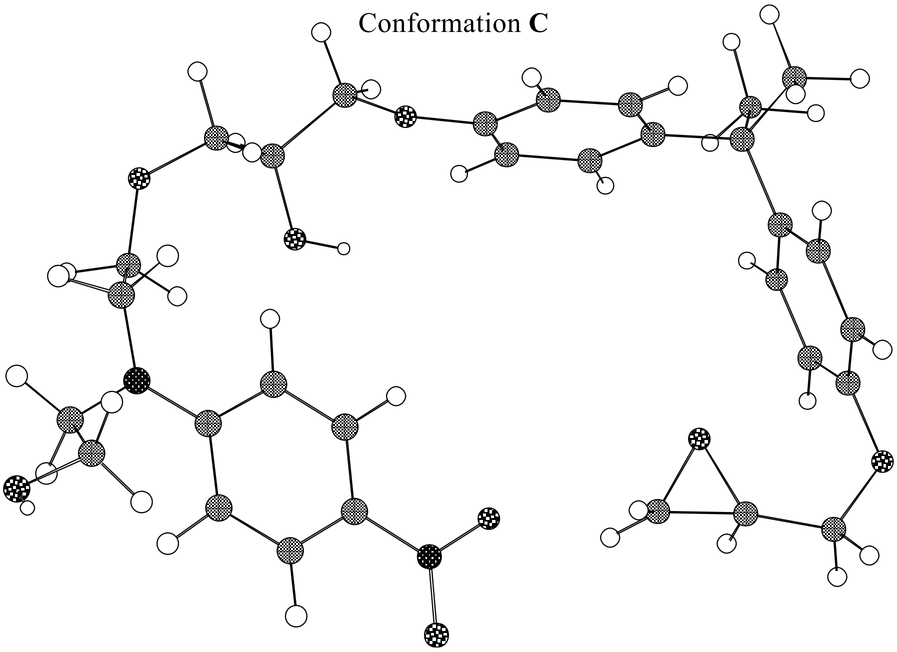


Figure 2. Model structures for oligomer **III**: conformation **T** has nearly transoidal bonds in the epoxy fragment; conformation **C** has a convoluted chain.

group of epoxy fragment and NO_2 group of the chromophore) is considerably less for **I** than for **III**; the dependence of β_{xxx} on the oligomer conformation is insignificant in the case of oligomer **I**.

Thus, one can conclude that to increase the oligomers hyperpolarizability compared to the inherent chromophore hyperpolarizability it is advisable to use the longest possible chains, and to insert bulk groups into the links nearest to the chromophore to prevent the oligomer chain convolution.

Table 3. Effect of conformation of chromophore fragment on its longitudinal hyperpolarizability.

Conformation	**A**	**B**	**C**	**D**
ΔE (kcal/mole)*)	0.0	0.3	0.8	3.7
φ (°)	162.8	158.6	159.5	–133.4
μ (**D**)*)	7.8	7.8	7.4	5.7
$\beta_{xxx} \cdot 10^{-30}$ (esu)	19.2	16.3	16.2	9.0

*)Δ**E** (kcal/mole) – relative values of the total energy of different conformations; μ(**D**) – the value of the dipole moment.

Let us consider now the results of calculations of the longitudinal hyperpolarizability for the most energetically favorable conformers of oligomers **I**, **II** and **III**. These structures are determined as a result of total optimization of their geometries. Here we analyze the dependence of β_{xxx} on the conformation of bearing chain. The obtained structure of the *p*-nitroaniline group is characterized by almost planar geometry, the out-of-plane angles of ring carbon atoms do not exceed 0.2°, NO_2 group also lies in this plane. The C–C bonds of ethoxy groups emerge from the ring plane insignificantly. The data in Table 3 demonstrate that the conformation of the chromophore fragment with maximum β_{xxx} has the least deviation of nitrogen bonds from planarity. For this conformation the φ angle differs noticeably from 180°, what reduces the hyperpolarizability value: $19.2 \cdot 10^{-30}$ esu compared to $21.2 \cdot 10^{-30}$ esu for the idealized planar structure. The considered systems possess a lot of conformational degrees of freedom. The potential energy surface for these systems obviously possesses manyfold shallow local minima, separated by small potential barriers. This fact results in a great flexibility and conformational mobility of these systems, and makes senseless the exact ascription of definite conformation to the oligomer chain. Hence, two key parameters are used to characterize the conformation: φ angle, indicating the nitrogen planeness, and the distance between the chain ends **R**. Parameter **R** is traditionally considered as a statistical characteristics of macromolecules conformations. That is why the use of **R** seems to be reasonable in the context of our task in spite of considering the systems with limited chain length. All the studied structures can be conventionally divided into favorable and unfavorable in β_{xxx}. The conformers are called favorable if their longitudinal hyperpolarizability exceeds $21.2 \cdot 10^{-30}$ esu (that is the β_{xxx} value of the isolated plane chromophore), otherwise, if $\beta_{xxx} < 21.2 \cdot 10^{-30}$

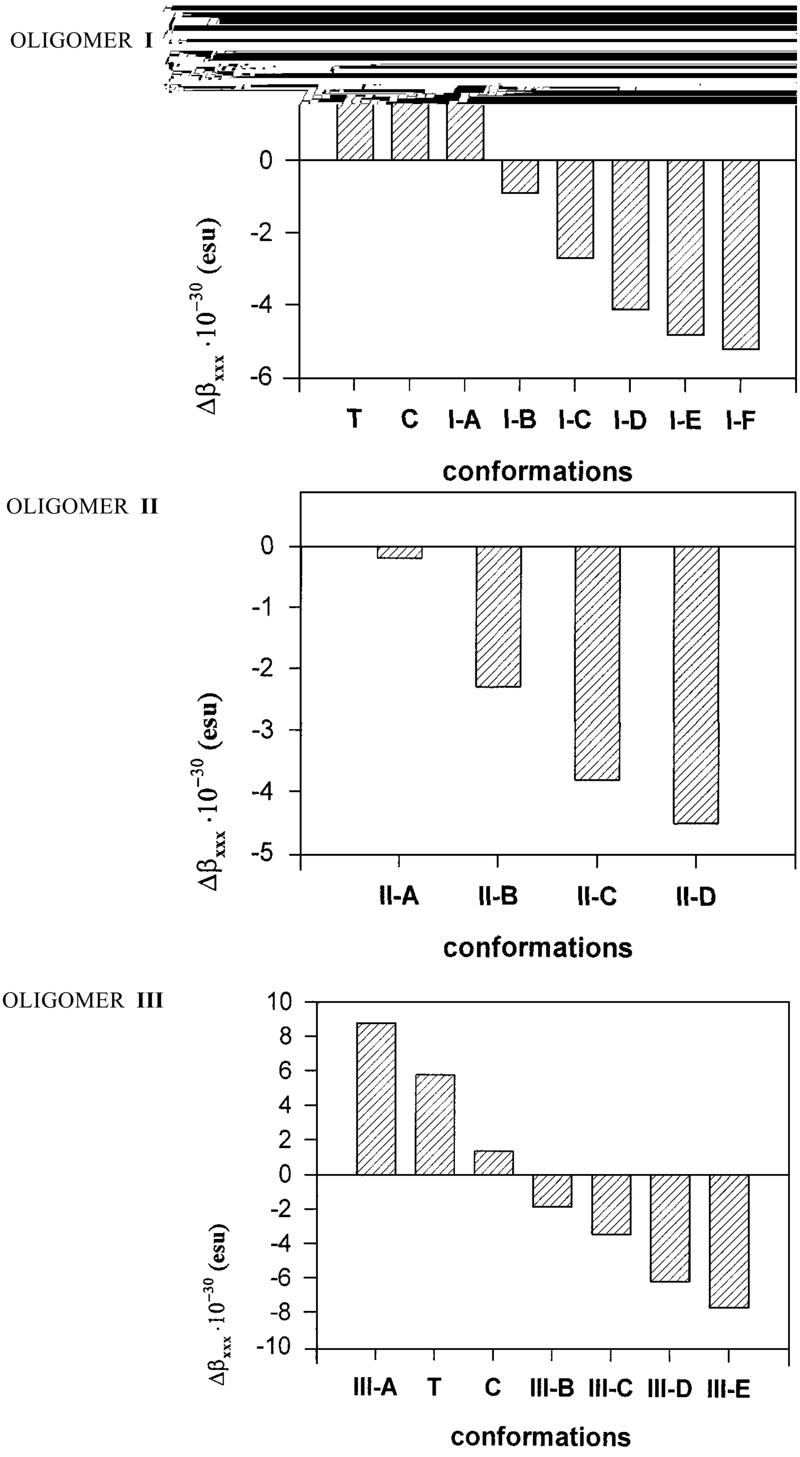


Figure 3. Histogram of the $\Delta\beta_{xxx}$ (the difference between β_{xxx} of oligomer and chromophore fragment) for a series of conformations of oligomers **I**, **II** and **III**.

Table 4. The effect of conformation of oligomer fragment on hyperpolarizability.

Conformation	Oligomer **I**						Oligomer **II**				Oligomer **III**				
	I-A	**I-B**	**I-C**	**I-D**	**I-E**	**I-F**	**II-A**	**II-B**	**II-C**	**II-D**	**III-A**	**III-B**	**III-C**	**III-D**	**III-E**
ΔE(kcal/mole)$^{*)}$	1.3	0.0	2.0	1.5	4.7	4.8	1.8	0.0	3.1	2.5	0.0	4.7	1.4	4.6	6.1
φ (°)	175.4	165.3	144.2	147.0	160.5	145.1	–171.3	–174.0	144.2	143.4	–155.5	–178.2	–176.8	–144.0	–146.7
R (**A**)$^{**)}$	8.1	12.2	11.2	8.9	12.5	12.8	15.5	14.0	15.2	15.0	21.9	10.5	11.1	23.1	17.1
μ (**D**)$^{*)}$	9.8	10.1	7.51	9.8	11.5	7.48	8.0	6.2	7.9	6.9	7.7	6.4	7.0	6.7	8.8
$\Delta\beta_{xxx}\cdot10^{-30}$ (esu)$^{***)}$	1.6	–0.9	–2.7	–4.1	–4.8	–5.2	–0.2	–2.3	–3.8	–4.5	8.8	–1.8	–3.4	–6.1	–7.6

$^{*)}$ **ΔE** (kcal/mole) – relative values of the total energy of different conformations; μ (**D**) – the value of the dipole moment.

$^{**)}$ **R** (**A**) – the distance between the chain ends: the end group of epoxy fragment and NO_2 group of the chromophore; μ (**D**) – dipole moment.

$^{***)}$ $\Delta\beta_{xxx}\cdot10^{-30}$ (esu) – the difference between β_{xxx} of oligomer and chromophore group, for the latter the value for ideal plane chromophore fragment being taken.

esu, they are called unfavorable. The values of β_{xxx} for several stable conformers of oligomers **I**, **II** and **III**, described by α,φ and **R**, are presented in Table 4. The values of $\Delta\beta_{xxx}$ (the difference between β_{xxx} of oligomer and chromophore) are shown in Fig. 3, demonstrating the pronounced effect of oligomer conformation on β_{xxx}.

The analysis of the favorable structures allows to conclude that requirements for optimal NLO structures formulated above on the basis of the data for model systems are mainly fulfilled: the configuration of bonds at nitrogen of the chromophore group is close to planar; more stretched molecular structures have higher β_{xxx} values; for longer oligomers **II** and **III** there occurs a certain correlation between β_{xxx} and **R**, for oligomer **I** this correlation nearly fails, because of the short oligomer chain. Besides, it is worth mentioning that favorable oligomer conformations preserve preferable structures of chromophore fragment, having maximum hyperpolarizability.

Thus, one may conclude that structure and conformation of oligomer chain may significantly affect the longitudinal hyperpolarizability of the chromophore. In particular, for epoxy systems studied here, the β_{xxx} values may be 1.4 times increased with conformation in certain cases. Further, more thorough study of this effect is needed to elaborate necessary recommendations for construction of polymer matrices bearing NLO chromophores. We hope that quantum chemical research of such kind will result in finding the guidelines for rational design of NLO cross-linked electrets.

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