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Relationship Between Electronic Structure and Nonlinear Optical Activity of Push-Pull Polyenes: Step Towards a Quantitative Treatment*

by M.B. Zuev[1], S.E. Nefediev[2] and J.-L. Bredas[3]

[1]*A.E. Arbuzov Institute of Organic and Physical Chemistry of Kazan Scientific Center,*
Russian Academy of Sciences, Arbuzov str. 8, 420088 Kazan, Russia; E-mail: mikhail@iopc.kcn.ru
[2]*Kazan State Technological University, Karl Marx str., 68, 420015 Kazan, Russia*
[3]*Department of Chemistry, University of Arizona, 1306 E. University Blvd., Tucson, AZ 85721-0041, USA*

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Mesomeric effect of substituents in stereoregular push-pull polyenes has been studied, bond length alternation being used for the monitoring of π-electron displacement along the polyene segment. Quantitative calibration of the π-donor and π-acceptor strength of various substituents has been performed with the special scale of substituents mesomeric constants. A simple quantum chemical technique for estimation of mesomeric constants has been developed. A simple additive equation describing the substituents mesomeric effect on bond length alternation in push-pull polyenes has been elaborated. Specific push-pull effect has been demonstrated to be the essential feature of push-pull polyenes. A qualitative relationship between the suggested mesomeric constants and longitudinal hyperpolarizability has been established.

Key words: push-pull polyenes, NLO chromophores, mesomeric model of substituents

Nonlinear optical (NLO) polymer electrets are prominent candidates as electro-optic materials for high-speed optoelectronic devices controlling light with electricity in fiber-optic communications [1–6]. The electro-optic response of these materials originates from the dipolar NLO chromophores, which are conjugated polyatomic groups with a large dipole moment and a high electronic hyperpolarizability. These groups are covalently incorporated into the chains of a polymer matrix, and their dipole moments are poled by an external electric field to produce a stable acentric system of the aligned NLO chromophores [7].

The bulk second-order nonlinearity of such system depends strongly on the NLO response of the individual chromophore group; its electronic and geometrical structures predetermining the NLO activity [8]. A strategy for designing chromophores with enhanced NLO properties has been the focus of many theoretical and experimental studies, performed during the last decade [9,10]. Two important milestones in the development of this strategy may be marked. A descriptive π-electron theory of nonlinear response in conjugated organic molecules has been formulated, and stereoregular

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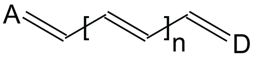
push-pull polyenes were predicted to be the most promising as advanced NLO chromophores [11–16]. More recently, the synthetic methodology was elaborated to obtain ring-locked *trans*-polyene chains with high thermal stability, and a series of push-pull polyenes with unsurpassed NLO activity has been synthesized [17–20].

A stereoregular push-pull polyene comprises a *trans*-polyene segment, terminated by π-electron acceptor and π-electron donor substituents; it may be sketched as



Here *n* is the number of unit cells producing the polyene segment; A and D designate the polyatomic fragments with π-electron accepting and π-electron donating groups at the double C=C bond of the substituent. Examples of terminal substituents in push-pull polyenes are given in Table 1. The amino and *p*-phenylamino groups are typically used as π-donors; the carbonyl and dicyanovinyl groups are exploited as π-acceptors. If the *n* value is reasonably large, the response of the push-pull polyene to an external electric field is predominantly conditioned by the polarization of the π-electron cloud along the conjugation path. The polarization in any other direction tends to vanish with the increase in *n*. That is why the NLO activity of push-pull polyenes is generally characterized by the longitudinal electronic hyperpolarizability β, estimated in the static limit. By definition, that is the component of the hyperpolarizability tensor along the *trans*-polyene chain axis, directed from the acceptor end of the chain to the donor one. The stereoregularity of the polyene segment provides a large amplitude of the π-electron displacement, induced by the longitudinal electric field component. This fact is of great importance for the nonlinear response formation. Since the unsubstituted *trans*-polyene possesses an inversion center, its intrinsic hyperpolarizability is equal to zero. The mesomeric effect of end substituents is exploited to produce acentric π-electron distribution in the polyene bridge. The ability of the substitutent to polarize the adjacent polyene segment is often termed its π-donor or π-acceptor strength. This quality is a key feature of a substituent in push-pull chromophores, however, up to now its quantitative calibration has not been proposed.

These statements form the basis of a descriptive π-electron theory of dipolar NLO chromophores developed mainly by Marder and his colleagues [11–16]. In this theory the NLO activity of a push-pull polyene is provided by the substituents, which contribute to β in two different ways. The first contribution comes from their own π-electron structures, which are mildly polarized by the longitudinal component of an external electric field. The second contribution originates from the *trans*-polyene segment polarized due to the mesomeric effect of the substituents. This contribution depends strongly on donor/acceptor (D/A) strength of the substituents, increases rapidly with the chain length *n*, and usually becomes dominant beginning from $n = 2$. This statement is indirectly supported by the qualitative correlation between β and *bond length alternation* (BLA) in the polyene segment; a decrease in BLA, due to enhanced mesomeric effect of the substituents, is usually accompanied with the increase in β [12]. This observation results in the using of BLA as a conventional measure of the strength of a given D/A pair of substituents. The pair is chosen to minimize the BLA in the middle of the polyene chain; it often results in the increase in β [12–16]. Marder *et al.* [11] have shown that the increase of β with n tends to saturation at definite value of n called the *saturation length*, n_S, depending upon the D/A strength of the substituents. The origin and the character of this dependence is not yet understood.

Design of push-pull chromophores includes the following actions. Starting from the vinyl group, coupled to the chosen π-donor or π-acceptor moieties, one may depict a great deal of acyclic and cyclic structures as potential D/A substituents. Each of the D/A pairs may be coupled then to the polyene chains of various lengths n. It is obviously impossible to test all these structures experimentally. The descriptive time-saving theoretical approaches are required to provide a preliminary choice of the strongest donors and acceptors and the determination of the saturation length n_S for a chosen D/A pair. This complicated task has not yet been completely fulfilled. A number of qualitative rules was formulated by Marder and co-workers for heterocyclic π-acceptors. The acceptor ability of carbonyl groups was shown to be essentially enhanced, when they are incorporated into the cycles, tending to gain the aromaticity upon polarization, the thiobarbituric cycle being a typical example [12–16]. However, these rules are not enough for a quick screening of possible structures; the overwhelming experimental efforts are still needed.

Two sub-problems are waiting for their solution, they are: i) the quantitative calibration of π-donor and π-acceptor strength of the substituents of the arbitrary structure by relevant mesomeric constants scale; ii) the elaboration of correlation equations, coupling the substituents mesomeric constants and polyene chain length with β. This contribution deals with the first of these sub-problems. In search for its solution we follow the general approach used by chemists for the quantitative description of the effect of substituents on the reactivity of a given functional group within a series of structurally related molecules [21].

We have studied the mesomeric effect of substituents in stereoregular push-pull polyenes using BLA for the monitoring of π-electron displacement along the polyene segment. We have started with the quantitative treatment of the substituent mesomeric effect on BLA in monosubstituted polyenes to calibrate the π-donor and π-acceptor strength of various substituents. The obtained scale of mesomeric constants below is referred to as the BLA-based one. The choice of the BLA for this purpose seems to be the most relevant, because the changes in BLA, caused by the D/A substituents, are the most descriptive from the chemical viewpoint. Besides, the qualitative correlation between β and BLA, stated by Marder *et al* [12], gives grounds to suggest that the BLA-based mesomeric constants would be appropriate for the description of the basic trends in β.

The mesomeric constants estimated using the data for these species are used then for the development of a simple additive equation, describing the substituents mesomeric effect on BLA in push-pull polyenes of various length n. A particular attention is paid to the quantitative description of the specific push-pull effect as the essential feature of push-pull polyenes with a relatively short π-conjugated segment. A qualitative relationship between the suggested mesomeric constants and longitudinal hyperpolarizability has been established.

METHODOLOGY

By definition the dipolar NLO chromophore is a conjugated polyatomic group covalently incorporated into a polymer matrix. Statistics of NLO polymers starts from the hyperpolarizability of individual chromophore groups as initial parameters of the theory; the effect of molecular environment is taken into account via local field corrections at the next level of sophistication [7]. It should be noted, that a free chromophore group is a virtual object; its electronic state is not a stationary one, it is a hypothetic *valence state*, reproducing the electron structure of this group in various molecules [22]. That is why a rigorous physical description of the individual chromophore group is impossible. Reasonable molecular models of chromophores are required to determine their structural and NLO characteristics.

To present the approach, used here, let us consider the chromophore (**I**) shown below:

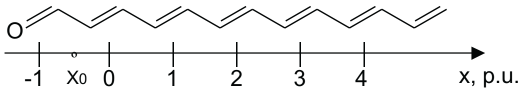
NLO chromophore (**I**) Molecular model, C_{1h} (**II**)

The valence dashes at nitrogen stand for the covalent bonds coupling the chromophore to a polymer chain, the nature of the latter being beyond the context of this study. The relevant molecular model (**II**) is constructed according to the following rules: the bonds at nitrogen are saturated by hydrogens, the planar structure of the conjugated system is assumed as it is the most probable for free chromophore group from the chemical point of view. The studied systems are denoted by the abbreviation *Di(n)Aj*, where *n* is a polyene chain length, *Di* and *Aj* stand for various π-donor and π-acceptor substituents according to Table 1; for the case of monosubstituted polyenes the abbreviation *Di(n)* and *Ai(n)* have been used. The BLA values of the studied systems are calculated by semiempirical AM1 technique [23] with optimization of all the geometrical parameters except torsion angles, which were specified to ensure the planarity of the conjugated segment. The longitudinal hyperpolarizabilities are calculated by TDHF technique [24] as incorporated in the GAMESS program package [25].

RESULTS AND DISCUSSION

We start with the quantitative treatment of the substituent mesomeric effect on BLA in monosubstituted polyenes. The mesomeric constants, estimated using the data for these species, are used then for the development of a simple additive equation describing the substituents mesomeric effect in push-pull polyenes of various length *n*.

Monosubstituted polyenes. Let us consider the *A1(4)* system as an illustrative example



The elementary units of polyene chain are numbered, starting from the one nearest to the substituent. Stereoregularity of *trans*-polyene makes feasible a characteristic unit of length equal to the distance between the centers of the double bonds, we call it below "a polyene unit" (1 *p.u.* has the order of 2.5 Å). Let us define *x* coordinate along the longitudinal molecular axis, according to the sketch presented above; this coordinate system sets the one-to-one correspondence between double bonds of polyene segment and integral values of x in the range from 1 to n, numbering unit cells of the polyene chain. This coordinate system is conventionally used to describe the mesomeric effect on BLA at various distances from the substituent. BLA may be defined now as a discrete function BLA(x), given for each unit of the polyene segment. For a given integer $x = 1,2,...n$ BLA(x) is defined as a difference between the half-sum of the boundary C–C bonds and double C=C bond belonging to this unit. The function BLA(x) may be presented in the form

$$\mathrm{BLA}(x) = \mathrm{BLA}^0(x) + \Delta\mathrm{BLA}(x)$$

where BLA^0 is the BLA value in an unsubstituted polyene of the same n, and ΔBLA is a perturbation in BLA, due to the substituent. The reference values of $\mathrm{BLA}^0(x)$ and BLA(x) at $x = 1,2...n$ have been calculated by AM1 technique. The obtained values of $\mathrm{BLA}^0(x)$ for unsubstituted polyene with $n = 12$ are presented in Figure 1. The values of BLA^0 are shown to be constant in the middle of the chain and increase rapidly when approaching their ends. The end effect demonstrates the cooperative character of conjugation in polyenes. It cannot be reduced to the pair interactions of neighboring C=C bonds. The AM1 value of BLA^0 in the middle of the chain is equal to 0.0962 Å, *this middle-of-chain* BLA^0 *value* is used below as a scale unit for BLA to avoid the uncertainty coming from the selection of the calculation technique and referred to as relative units *(r.u.)*. The phenomenological approach, being developed here, does not take into account the details of the electronic structure of the substituent. The latter is formally considered as a point source of perturbation in BLA, and characterized by

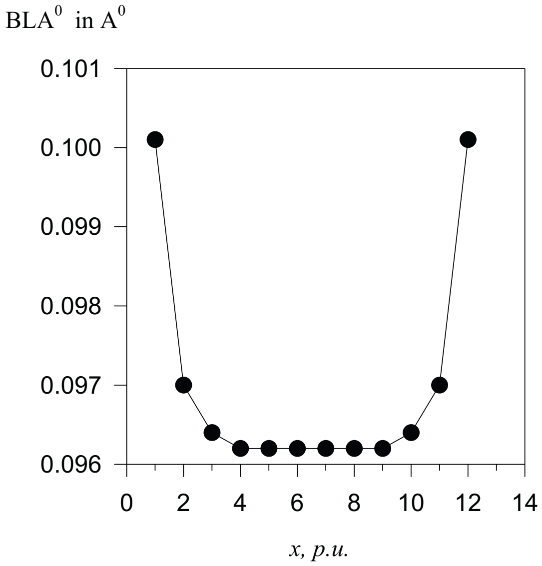


Figure 1. Bond-length alternation of nonsubstituted *trans*-polyene.

two parameters: x_0 coordinate, which specifies the positions of the source on x axis (see the sketch above), and by mesomeric constant σ, representing π-donor or π-acceptor strength of a substituent with respect to the standard chosen. The mesomeric effect of substituent on BLA in polyene segment is described by a smooth function ΔBLA(x-x_0), which depends upon σ as a parameter and reproduces reference (quantum-chemical) data for integer values of x.

The effect of substituents on BLA in monosubstituted polyenes is illustrated by Figure 2. Comparing the curves for A1 and A2, which differ only by the orientation of C=O group with respect to the end C=C bond, one may see that in both cases ΔBLA tends to zero with increase of x, reaching zero after $x = 4$. This attenuation of mesomeric effect seems to be caused by relaxation of the σ-electron core of polyene segment accompanying the π-electron displacement.

We have suggested that π-donor or π-acceptor strength of the substituent determines the range of its action. To confirm this assumption, let us compare ΔBLA(x) functions for two acyclic π-acceptors: carbonyl A1 and nitro A4 groups are presented in Figure 2. It may be seen that the perturbation from a stronger substituent A4 attenuates slower and becomes equal to zero only after the fifth unit of the polyene segment. To construct a convenient scale for mesomeric constants it is necessary to find one-parametric smooth approximation for ΔBLA, the parameter being proportional to the range of substituent action. In the course of numerical experiments we have found the following equation to be the best one:

$$\Delta BLA(x) = \tanh\left(\frac{x - x_0}{\eta_0 \sigma}\right) - 1 \qquad (1)$$

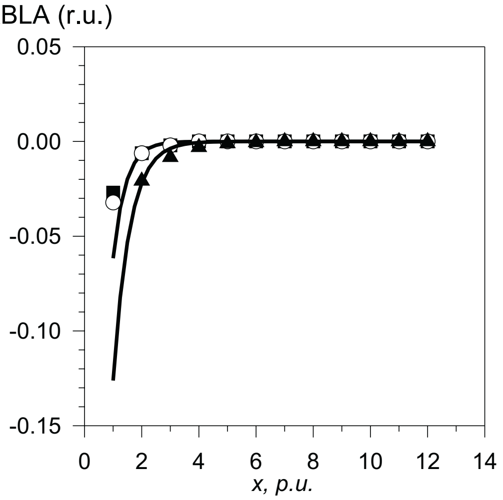
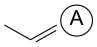
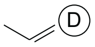
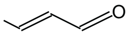
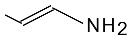
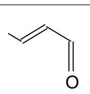
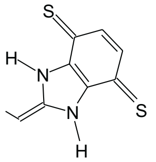
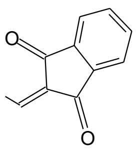
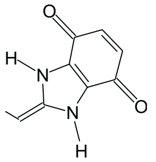
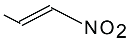
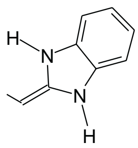
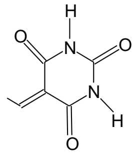
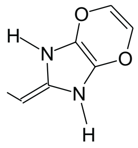
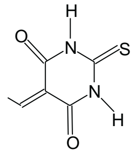
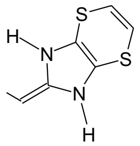
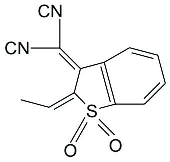
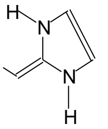
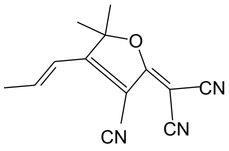
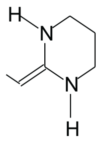


Figure 2. Effect of substituents on the bond-length alternation in monosubstituted polyenes. White circles correspond to A2, black squares stand for A1 and black triangles denote A4. Continuous line is obtained according to (1). The ΔBLA is given in middle-of-chain BLA^0 units.

Before turning to the discussion of the constants of this equation, it is worth mentioning that any scale of the substituent constants is determined with respect to two selected functional groups. The first one is the standard for comparison; in our case it is unsubstituted vinyl group, its mesomeric constant is assumed to be zero. The second one defines the unit of the scale. We have chosen the substituent A1 for this purpose. In so doing η_0 coefficient equals 0.87 *p.u.* and σ is a dimensionless mesomeric constant presenting the strength of the substituent with respect to the standard. It must be stressed that σ describes only the absolute value of the effect, but not the sign; the latter is defined by the direction of the π-electron displacement and may be easily obtained from qualitative chemical considerations. The coordinate of the source of perturbation x_0 depends upon the nature of unsaturated fragment, separating the polyene segment from π-donor and π-acceptor moieties incorporated into substituents. If only one C=C bond plays the role of a conductor of perturbation, x_0 is assumed to -0.5 *p.u.* This value is somewhat arbitrary, but our numerical experiments have shown that when x_0 changes in the range from -0.25 to 0.75 *p.u.*, only the scaling factor η_0 is affected, but not the σ constant of the substituent.

When defining the mesomeric constant of the substituents, the most complicated problem is the separation of different intramolecular interactions [21]. According to the additivity principle, ΔBLA is a sum of contributions from mesomeric, inductive and steric effects of a substituent. As the range of steric and inductive actions is much smaller than that of conjugative one, we assume that the contributions from the corresponding effects to BLA become negligibly small, starting from the second unit of polyene chain. The curves in Figure 2 confirm this assumption. It can be seen, that ΔBLA for stereoisomeric functionalities A1 and A2 coincide at all x values except $x = 1$, corresponding to the unit cell nearest to the substituent. These differences may be due to steric and inductive effects, depending on the substituent geometry to a greater extent than the mesomeric one. Mesomeric constants are obtained here by a standard least-squares fit on the basis of quantum-chemical data for monosubstituted *trans*-polyene with $n = 12$. In doing so we excluded the reference ΔBLA(1) value from the fit to separate the contributions from steric and inductive effects. The obtained mesomeric constants of various substituents are presented in Table 1. (1) reproduces the reference data with the accuracy of 0.003 *r.u.*, that is 5% in average. For a design of molecular structures with high longitudinal hyperpolarizability, the cyclic functionalities with two π-donor or π-acceptor moieties at the C=C bond of the substituent seem to be of most interest. Usually such functionalities have an intrinsic π-electron structure, being capable either to strengthen or to weaken the mesomeric effect of the moieties. The effect of the cycle structure on the strength of π-donor substituent follows rather simple qualitative regularities. The integration of amino groups into a cycle without intrinsic conjugation system seems to be the most preferable, the presence of the intrinsic conjugation system always results in the decrease of substituents σ.

Table 1. Structural formulas and mesomeric constants of substituents.

Code		σ	**Code**		σ
A1		1.00	**D1**		1.34
A2		1.00	**D2**		1.40
A3		1.16	**D3**		1.41
A4		1.28	**D4**		1.48
A5		1.41	**D5**		1.50
A6		1.48	**D6**		1.55
A7		1.57	**D7**		1.65
A8		1.58	**D8**		1.67

The case of π-acceptor functionalities is much more complicated. Intrinsic conjugation system of the cycle may weaken as well as strengthen the mesomeric effect of carbonyl groups, the strengthening occurs only in the structures containing additional acceptor moieties. Derivatives of barbituric and thiobarbituric acids (A5 and A6 correspondingly) exhibit the most pronounced mesomeric effect, in accordance with qualitative statements of Marder and co-workers [11–16]. The largest σ corresponds to A7 and A8. The NLO polymers based on the chromophores with these π-acceptor substituents have been studied experimentally and have exhibited an outstandingly high electro-optic response [4,18]. This fact indirectly confirms the validity of the approach elaborated here.

Push-pull polyenes. The quantitative treatment of mesomeric effect in push-pull polyenes is based on the following intuitive consideration. Because of attenuation of π-electron displacement along the polyene segment, each substituent can be characterized by a finite range of action, proportional to its σ. In the framework of developed descriptive theory, the substituent range of action may be defined as the distance R (in *p.u.*) between the point source of perturbation and the point x, where ΔBLA reaches a given infinitesimal value ε. It follows from (1) that

$$R = k\sigma, \quad k = \eta_0 \tanh^{-1}(1-\varepsilon) \tag{2}$$

Assuming that $\varepsilon = 0.5\cdot 10^{-5}$, we obtain $k = 5.5$ *p.u.* in accordance with the qualitative considerations made above. The number of polyene unit cells, affected by the substituent, is equal to *R-1.5*, rounded to the nearest integer. It is easy to suggest, that when the chain length n has the order of $R_A + R_D$ the effect of the end substituents summarizes; it may be described by:

$$\Delta BLA(x) = \tanh\left(\frac{x - x_0}{\eta_0 \sigma_A}\right) + \tanh\left(\frac{n + 1 - x_0 - x}{\eta_0 \sigma_D}\right) - 2 \tag{3}$$

The analysis of quantum-chemical data confirms this assumption. However, when n is notably smaller than $R_A + R_D$, nonadditive *push-pull effect* arises. From the chemical point of view the origin of this effect is in the mutual influence of the substituents, resulting in the enhancement of their mesomeric strengths. The analysis of the reference data shows that the push-pull effect may be described by:

$$\Delta BLA(x) = \tanh\left(\frac{x - x_0}{\eta_0 \Sigma_A}\right) + \tanh\left(\frac{n + 1 - x_0 - x}{\eta_0 \Sigma_D}\right) - 2 \tag{4}$$

where Σ_A and Σ_D are the actual mesomeric constants, accounting for the push-pull effect. They are defined as

$$\Sigma_A = \sigma_A + \sigma_D \exp\left(-\alpha \frac{n}{\sigma_A + \sigma_D}\right) \qquad \Sigma_D = \sigma_D + \sigma_A \exp\left(-\alpha \frac{n}{\sigma_A + \sigma_D}\right) \tag{5}$$

where α is a constant equal to 1.1. To explain the reasoning behind (5), let us note, that the value of Σ_A must depend upon the inherent mesomeric strength of the other terminal substituent (σ_D in this case), and tends to σ_A with n reaching $R_A + R_D$. The above given value of $\alpha = 1.1$ corresponds to the negligible uncertainty in Σ, which was postulated to be 0.005. Further refinement of α by the least-square-fit did not change this value. Figure 3 demonstrates the quality of the suggested additive equation, which seems to be sufficient for the quantitative estimation of BLA in push-pull polyenes. The approach developed here may give the basis for the design of molecular structures with high β. To illustrate this assumption, let us consider the dependencies β(*n*) calculated by TDHF technique with AM1 Hamiltonian (see Figure 4). The β value is expressed in relative units defined with respect to the reference molecule, which is the analogue of the strongest ring-locked NLO chromophore known up to now [18]:

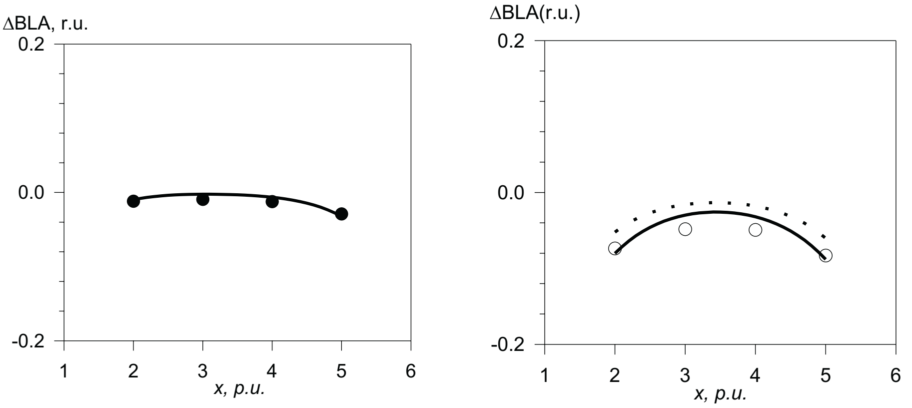


Figure 3. Nonadditive *push-pull effect* in donor/acceptor substituted polyenes. Black circles correspond to A1(6)D1 and white circles stand for A8(6)D7. Dotted line is obtained according to Equation (3). Continuous line is obtained from Equations (4 and 5). The ΔBLA is given in middle-of-chain BLA^0 units.

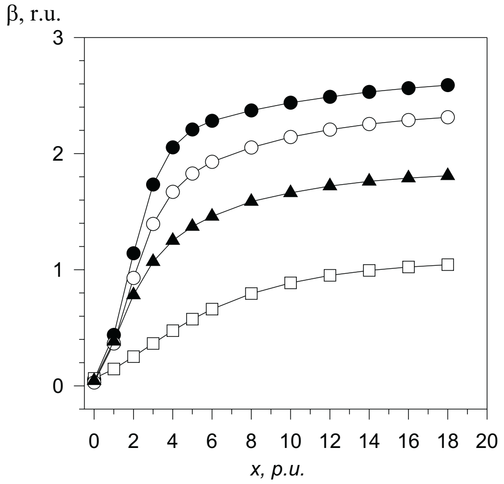
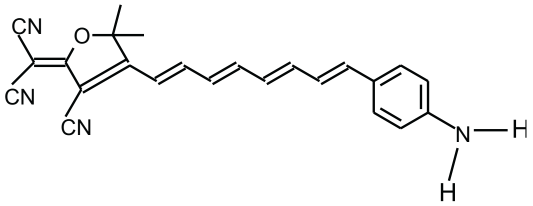


Figure 4. Dependences of the longitudinal hyperpolarizability on chain length *n* in push-pull polyenes with various substituents. White squares correspond to A1(n)D1; black triangles stand for A5(n)D3; white circles denote A5(n)D7; black circles correspond to A8(n)D7. The β values are expressed in relative units defined with respect to the reference molecule shown on the sketch (see the text).



It may be seen that there is an impressive qualitative correlation between mesomeric constants σ of the substituents and the longitudinal hyperpolarizabilities β. The stronger the D/A pair, the higher are the corresponding $\beta(n)$ values, and the quicker $\beta(n)$ curve tends to saturation. The correlation analytic equations, representing β as a function of n, σ_A, and σ_D are now under elaboration and will be presented elsewhere.

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