Effects of an Applied Field on the Structure of Finite Polyenes

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We investigate the effect of an applied field, the internal molecular field produced by donor−acceptor groups, as well that of an effective field by the environment, on the electronic properties and geometric structure of substituted polyenes of finite length. We use analytically tractable methods to study (a) the effect of static field on the bond length alternation (BLA) of finite polyene rings and (b) the effect of static field on even and odd open chains. We find that the field drives the rings to lower BLA and that odd chains in a static field can show reversal of BLA through the equal bond length limit.

1. Introduction

Organic molecules and polymers with extended π-conjugation have attracted attention for optoelectronic and photonic applications because of their large nonlinear optical (NLO) responses.[1−3] Optimization of the performance of materials for those applications has been the focus of extended research.[2,4,5] Central to the problem of optimization lies the question of the relation between structure, both chemical and geometric, and the electronic and optical properties, both linear and nonlinear.

In particular, donor−acceptor substituted polyenes have been suggested as an important class of organic molecules for large second-order NLO responses.[4−6] Most studies have focused on the influence of the donor−acceptor strength in a two-state model[7] in which the response increases as the difference in the ground- and excited-state dipole moment matrix elements increases. It has been recently found, however, by Marder et al. that, in small donor−acceptor polyenes, geometric structure and optical responses (both linear and nonlinear) are connected in a simple way.[8−10] Their idea is that the internal field of the molecule (due to the donor−acceptor as well as the environment such as the polarity of the solvent) controls its structure and hence the optical response. Numerical calculations support their conjecture.[11] The π-electron bond length alternation (BLA), the average difference between adjacent carbon−carbon bonds, has been chosen as the parameter to describe the geometrical structure. The change of BLA from its original value (neutral donor−acceptor system) through the equal bond length situation (BLA $= 0$) to its reversal of magnitude (charge-separated system) is correlated to the applied field and hence to the optical properties.

To elucidate the origins of these results, we study the effect of a static applied field on the geometry of systems that are modeled after the donor−acceptor polyenes. The models are chosen to contain the essence of the physical systems and can still be solved analytically. We use Hückel theory, which has been widely used to describe the qualitative behavior of conjugated molecules.[12]

First, we study the effect of an applied field on the energy spectrum and structure of finite even-membered rings of any length. Within Hückel theory and periodic boundary conditions, we find that the presence of the field drives the system toward lower BLA. We then lift the periodic boundary condition restriction and compare the effect of the field on even and odd linear hydrocarbon chains. We consider the simplest possible cases, the three- and four-carbon linear polyenes, and obtain functional forms between the field and displacement of atoms from equilibrium. We find those forms to differ, reflecting the different symmetries of the two systems. Although the odd system's ground-state energy contains odd power terms in field and displacement, the even one contains only even ones. We show that this result holds for any finite length open-ended chain. We conclude that the BLA can reverse signs by passing through zero (the equal bond length case) only in the case of the odd positive ions. It is a consequence of the inherent degeneracy of the ground state of odd chains, which is absent in the even case for finite systems. This result appears when the proper boundary conditions are imposed; if periodic boundary conditions or the infinitely long limit are applied, this end effect disappears.

In section 2 we consider the effect of the applied field on even-membered rings where periodic boundary conditions are meaningful. We look at the stability of the bond-alternating configuration in the presence of the field, through the second derivative of the ground state, similar in spirit to the calculation of Longuet-Higgins and Salem.[13] We find that the field favors the equal bond legth chain, i.e., disfavors bond alternation. In section 3.1, we compare the ground-state energy and equilibrium displacement of three- and four-carbon linear chains in the presence of the field with open-end boundary conditions. We show that the odd positive ion exhibits BLA reversal. In section 3.2 we show that the different behavior of odd and even chains persists for any finite chain length. In section 4 we comment on the physical origin of our results.

2. Bond Alternation in Finite Cyclic Polyenes in Presence of an Applied Field

To explore the effect of the applied field on the bond length alternation, we take advantage of periodic boundary conditions to obtain exact results. Thus, we begin by even carbon polyenes rings of finite length with general form $C_{4n+2}H_{4n+2}$. We express the ground-state energy in terms of the displacement of the

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carbon atoms from the equal bond length configuration x and the applied field f. The calculation proceeds in the spirit of that of that of Longuet-Higgins and Salem[13] (LHS). The σ bond energy as a function of x is given by $(1/2)\omega^2x^2$, favoring equal bond lengths ($x = 0$); the π contribution is given by

$$E_g^\pi(x,f) = E^\pi(x,0) - \frac{1}{2}\alpha(x)f^2 \tag{1}$$

where f is the applied field, x is the bond order alternation parameter, and $\alpha(x)$ is the polarizability as a function of x. LHS[13] found that

$$\left(\frac{dE_g^\pi}{dx^2}(x,0)\right)_{x=0}$$

was negative, and so the π energy favored bond alternation (i.e. $x \neq 0$). The question we ask is whether the field-dependent term in eq 1 favors $x = 0$ (i.e., $(d^2\alpha/dx^2)_{x=0} < 0$) or $x \neq 0$ (i.e., $(d^2\alpha/dx^2)_{x=0} > 0$). In the former case, a competition of two effects is created so that one could imagine that for certain limits of f the favorable form becomes the equal distant bond length chain. In the latter, the field acts in the same direction as bond alternation, thus not providing a means of achieving BLA = 0 or reversing the BLA by that method. We will show that the former is the case here.

As in LHS, the ground-state energy is taken to be the sum of the occupied orbitals (for a ring of $4N + 2$ atoms)

$$E_g^\pi(x,0) = 2\sum_{j=-N}^{N}\epsilon_j$$

where

$$\epsilon_j = \sqrt{\beta_1^2 + \beta_2^2 + 2\beta_1\beta_2\cos[2j\pi/(2N+1)]} \tag{2}$$

We denote the resonance integrals across the double (β_2) and single (β_1) bonds by

$$\beta_2 \leq \beta_1 < 0 \tag{3}$$

We express alternately increasing and decreasing bond lengths by modifying the resonance integrals so that

$$\beta_1 = \beta_0 e^{-x}, \quad \beta_2 = \beta_0 e^{x} \tag{4}$$

where x is a small positive quantity (β_0 is negative). The actual change in bond length is equal to ax, where a is a positive parameter. The second derivative of $E_g^\pi(x,0)$ with respect to x was found[13] to be negative and increases as $N \ln N$.

To see the effect of the field on the energy as a function of x, we now proceed to calculate the second derivative of the linear polarizability with respect to x. The standard expression from perturbation theory for α

$$\alpha = 2\sum_e{}' \frac{|\langle\psi_g(x)|\mu|\psi_e(x)\rangle|^2}{E_e(x) - E_g(x)} \tag{5}$$

where $\langle\psi_g(x)|\mu|\psi_e(x)\rangle$ is the transition moment matrix element between an excited state and the ground state. The prime denotes a restricted sum, due to exclusion of the ground state. For consistent use of periodic boundary conditions in finite systems, the periodic representation of the dipole moment operator is the appropriate one.[14] For a ring of $4N + 2$ carbon atoms,

$$\hat{\mu} = \frac{e(2N+1)l}{2\pi}\left[\sum_{j=-n}^{n}\left\{\cos\left(\frac{2\pi j}{2N+1} + x_1\right)|2j\rangle\langle 2j| + \cos\left(\frac{2\pi(j+1/2)}{2N+1} + x_2\right)|2j+1\rangle\langle 2j+1|\right\}\right] \tag{6}$$

where $l = 2l_0$ is twice the equal bond length magnitude and x_1 and x_2 are angles defined in such a way that the single and double bond lengths are given for small x by

$$l_s = l_0 + ax$$

and

$$l_d = l_0 - ax$$

We find

$$x_1 = -x_2 = \frac{ax2\pi}{(2N+1)l}$$

Since the HOMO to LUMO transition carries most of the oscillator strength, we consider only this excitation in the sum. α now becomes

$$\alpha(x) \simeq 2\frac{|\langle\psi_{\mathrm{HOMO}}|\hat{\mu}|\psi_{\mathrm{LUMO}}\rangle|^2}{\Delta E} \tag{7}$$

The appropriate wave functions are now those for $j = N$

$$\psi_{\mathrm{HOMO}} = \frac{1}{\sqrt{4N+2}}\sum_j\{e^{ij\theta_N - i\gamma_N}|2j\rangle + e^{i(2j+1)\theta_N/(2+i\gamma_N)}|2j+1\rangle\} \tag{8}$$

where

$$\theta_N = \frac{2\pi N}{2N+1} \simeq \pi$$

and

$$\gamma_{\mathrm{HOMO}}(x) = \frac{1}{2}\arctan\left(\tanh x \tan\frac{\pi N}{2N+1}\right) = -\gamma_{\mathrm{LUMO}}(x)$$

From eq 2, we obtain for the energy difference

$$\Delta E = 2|\beta_0|\sqrt{2\cosh 2x + 2\cos\frac{2N\pi}{2N+1}} \tag{9}$$

Substituting eqs 6, 8, and 9 into eq 7, for a small displacement of bonds x,

$$\alpha(x) = \frac{e^2l^2(2N+1)}{8\pi^2|\beta_0|\sqrt{2\cosh 2x + 2\cos\frac{2N\pi}{2N+1}}} \left|\left[\sum_j\cos\left(\frac{2\pi j}{2N+1} + x_1(x)\right)e^{-2\pi j/(2N+1)} - \sum_j\cos\left(\frac{2\pi(j+1/2)}{2N+1} + x_2(x)\right)e^{2\pi(j-1)/(2N+1)}\right]\right|^2 \tag{10}$$

The sums in eq 10 can be done, and we find

$$\alpha(x) = \alpha(0) - \frac{e^2 a^2 x^2}{2|\beta_0|\left[x^2 + \dfrac{\pi^2}{(2N+1)^2}\right]^{1/2}} \tag{11}$$

Therefore, $[\alpha'']_{x=0} < 0$ and

$$E_{\mathrm{g}}^{\pi}(x,f) = E_{\mathrm{g}}^{\pi}(x,0) - \frac{1}{2}(\alpha(0) + [\alpha''(x)]_{x=0}x^2)f^2 \tag{12}$$

so that the external field works in the opposite direction to the π-electron energy (i.e., the second derivative with respect to x of the π-electron energy is negative, and the second derivative of the energy due to the electric field is positive). That is, the electric field effect favors equal bond lengths.

3. Odd vs Even Finite Linear Polyenes in Presence of an Applied Field

3.1. Three- and Four-Carbon Chains. We investigate the effect of the applied field on the structure of donor−acceptor finite polyenes further, through the bond alternation parameter. In particular, we consider odd as well as even open finite chains. The periodic boundary condition is no longer appropriate. In this section, we begin by considering the simplest case, three- and four-carbon open-chain molecules, and we obtain the ground-state energy and dipole moment as a function of the bond alternation parameter x and the applied field f. We find that the functional dependence is quite different, reflecting the different symmetries of the two systems. In particular, although the properties of the even system contain only even powers in fx, those of the odd also contain odd power terms, such as xf. Motivated by the above result, we study further the radical as well as the positive ion and find that BLA reversal through the equal bond length case occurs for odd positive ions. We show that the results of ref 11 are qualitatively reproduced for this case.

We follow the notation introduced in section 2. In particular, for the radical in site representation where the charge of an electron e is 1 and f is the applied field,

$$H = \begin{pmatrix} f & \beta_0 e^{-x} & 0 \\ \beta_0 e^{-x} & 0 & \beta_0 e^{x} \\ 0 & \beta_0 e^{x} & -f \end{pmatrix} \tag{13}$$

For $x = 0$, in terms of $y = f/\beta_0$ the three orbital energies are

$$\lambda^0 = 0 \qquad \lambda^0_{\pm} = \pm\sqrt{y^2 + 2}$$

The first-order corrections in x are

$$\epsilon_{\pm} = \frac{-2yx}{(y^2 + 2)}$$

$$\epsilon_0 = \frac{4yx}{(y^2 + 2)}$$

On the other hand, for the four-membered chain,

$$H = \begin{pmatrix} 2f & \beta_0 e^{-x} & 0 & 0 \\ \beta_0 e^{-x} & f & \beta_0 e^{x} & 0 \\ 0 & \beta_0 e^{x} & -f & \beta_0 e^{-x} \\ 0 & 0 & \beta_0 e^{-x} & 2f \end{pmatrix} \tag{14}$$

The orbital energies are now (again in terms of $y = f/\beta_0$)

$$\epsilon_{1,2} = \pm\frac{1}{2}\sqrt{10y^2 + 4\cosh 2x + 2e^{-2x} + 2S}$$

$$\epsilon_{3,4} = \pm\frac{1}{2}\sqrt{10y^2 + 4\cosh 2x - 2e^{-2x} + 2S}$$

where $S = (9y^4 + e^{4x} - 12\sinh 2x + 30y^2e^{-2x} + 4)^{1/2}$. There is no term linear in xf. We will show in section 3.2 this difference in behavior to persist for longer chains.

Let us consider the three-carbon open chain further. To mimic a donor−acceptor substituted polyene, we replace f by $g = -\Delta + f$ in the Hamiltonian matrix. Thus, at zero applied field, site 1 has energy $-\Delta$ and site 3 energy $+\Delta$. In the presence of the field f, the site energies are transformed to $+g$ and $-g$, respectively. Note that the energies retain the same form, with f replaced by g so that g is the effective field on the system.

Now consider a three-electron, three-carbon chain. The total π energy in the Hückel model is then

$$E^{\pi}_{N=3}(x,f)/\beta_0 = 2\epsilon_+ + \epsilon_0 = +2\sqrt{y^2 + 2} + O(g^2x^2)$$

where $y = g/\beta_0$. We can also compute the dipole moment of this system to this order and find (as a function of field)

$$\mu(x;f) = 2\left[\frac{-y}{(y^2+2)^{1/2}} + \frac{2x(2-y^2)}{(y^2+2)^2}\right] + \frac{4x(y^2-2)}{(y^2+2)^2}$$

$$= \frac{-2y}{(y^2+2)^2} + O(g^2x^2) = -\left(\frac{\partial E^{\pi}}{\partial y}\right)_x$$

Thus, μ is an even function of x for small x. If we now consider a two-electron, three-carbon chain, the total energy and dipole moment become

$$E^{\pi}(x,f)/\beta_0 = E^{\pi}_{N=3}(x,f)/\beta_0 - \epsilon_0 = 2\epsilon_+ = +2\sqrt{y^2+2} - \frac{4xy}{(y^2+2)}$$

and

$$\mu(x;f) = \frac{-2y}{(y^2+2)^{1/2}} - \frac{4x(y^2-2)}{(y^2+2)^2}$$

The σ electron energy is given by

$$E^{\sigma}(x,f) \approx \frac{1}{2}\omega^2 x^2$$

so that the equilibrium value of x as a function of field is given by

$$x_{\mathrm{eq}} = \frac{4y}{\omega(y^2+2)} = \frac{4(f-\Delta)/(\beta_0\omega)}{(f-\Delta)^2 + 2} \tag{15}$$

One can easily see that the same result holds for a four-electron, three-carbon chain. Thus, for $|f - \Delta| \leq (2)^{1/2}$, the bond alternation, x_{eq}, is nearly a linear function of applied field and is zero at $f = \Delta$. This is similar to the relationship found in ref 8. Moreover, x_{eq} saturates as a function of y and then goes to zero again for large y. In the intermediate range, however, x_{eq} has a slightly sigmoidal shape as a function of field (see Figure 1 of ref 11). We now calculate the molecular polarizabilities as a function of field by differentiating E^{π} with respect to y. Note that x_{eq} is given by eq 15 so that, for practical purposes, in the region $|y| < (2)^{1/2}$, y is proportional to x_{eq}. The molecular polarizabilities α, β, and γ are further derivatives of $\mu(x,f)$ with respect to f. Since f and x_{eq} are linearly related, the polarizabilities can be considered to be further derivatives with respect to x_{eq}, leading to forms for the polarizabilities in agreement with those found in refs 8 and 11.

By examining any positive or negative ion odd-atom donor−acceptor system, we find the same qualitative behavior as above. The molecules considered in ref 11 are 11-atom systems, with (effectively) 10 π electrons.

We see from this analysis that the qualitative results of refs 8 and 11 are present already in the Hückel model of π-electron molecules.

3.2. Generalization for Any Finite Chain of Length *N*. In the previous section we found that the three-carbon atom molecule behaves differently from that of four carbons. The results were a direct consequence of the absence of linear terms in the field f and displacement x in the four-carbon case. Specifically, the energy level at the zero of energy was shown to be proportional to xf, which caused the BLA reversal as explained in section 3.1. Here, we demonstrate that these two results hold for any linear chain of length N when the open end conditions are imposed.

In the Appendix, we find the expansion of the secular determinant for tridiagonal Hamiltonian matrices of the form considered here, in powers of the effective fields Δ_i at the sites. The result is given in eq A4. Here, we show that the secular determinant for even and odd chains is different; for odd chains the determinant has a term linear in the Δ_i, while for even chains, it has no linear term. The Hamiltonian for even chains follows that of eq 14, while those for odd follows that of eq 13. Here, the Δ_i's are the field terms and $\mathbf{M}^0$ is the Hamiltonian for $f = 0$. Note that the diagonal terms of $\mathbf{M}^0$ contain the eigenvalues $\{\lambda\}$ of $\mathbf{M}$. We are interested in the first-order correction of the eigenvalues to the field (the linear response), so we can truncate the expansion in eq A4 after the first two terms.

We first consider even chains, and we show that the linear term to the field vanishes. It is easy to see from the matrix $\mathbf{M}^0$ by inspection that the cofactors $\mathbf{M}^0(i|i)$ of complementary sites are identical:

$$\mathbf{M}^0(i|i) = \mathbf{M}^0{}_{(N+1-i|N+1-i)}$$

so that the term vanishes because

$$\Delta_i = -\Delta_{N+1-i}$$

by construction.

We now turn to the odd chains. The Δ_i's are now incrementing in absolute value from the center of the chain where $\Delta = 0$. We can distinguish two types of odd chains: those for which the two half-chains are even and those for which the two halves are still odd. In the first case the cofactors of the complementary sites (that is, sites j and $N - j + 1$) are identical. Those terms cancel, since they are multiplied by the field, which is equal in magnitude but opposite in sign. Only the two end cofactors remain, $\mathbf{M}^0(1|1)$ and $\mathbf{M}^0(N,N)$. The constant term of the polynomial equation, independent of λ goes like $\sinh x \approx x$. Now we can rewrite the polynomial equation in powers of λ, which is of order N, with contributions $g_j(x)$ from $|\mathbf{M}^0|$ and $g'_j(x)$ from the determinant of the cofactors $|\mathbf{M}^0(i|i)|$:

$$\lambda^N[g_N(x) + fg'_N] + ...\lambda[g_1(x) + fg'_1] + [g_0(x) + fg'_0]$$

where $g_0(x) = 0$ and $g'_0 \approx x$. We can obtain the first-order corrections by substituting $\lambda^j = \lambda^{j,0} + \delta_j$. For the zeroth eigenvalue, $\lambda^{j,0} = 0$, and so we obtain

$$\delta_0 = fx/[g_1(x) + fg'_1(x)]$$

The rest of the argument then is identical to that of section 3.1. The other types of odd chains exhibit a similar behavior, but the constant term has a more complex functional dependence on x.

4. Conclusions

In this work, we have investigated the effect of an applied electric field on the energy spectrum and the structure of finite polyene systems. Changes in structure have been studied through the bond length alternation, or the extent of the difference between single and double bonds across the conjugated chain. Our work was motivated by recent conjectures that the BLA plays an important role in determining the nonlinear optical response in conjugated molecules with strong electron donor and acceptor substituents.[11] The applied field was intended to mimic the effect of the donor−acceptor groups as well as the surrounding medium.

Following Longuet-Higgins and Salem,[13] we found that the field-dependent term in the second derivative of the ground-state energy decreases the bond alternation effect; that is, it acts in the direction opposite from that of the π-electron energy term calculated by LHS. These calculations concerned even cyclic polyenes with periodic boundary conditions.

We then compared the functional form of the energy as a function of the field and BLA in even and odd chains and found a striking difference between the two. The BLA reversal may be obtained in the odd positive or negative ions, while it is absent in the even chains. The physical reason for this is that in the odd chains there is an inherent degeneracy in the ground state. This is not the case for even finite chains. This effect is lost if one applies the infinitely long limit or periodic boundary conditions.

In conclusion, in the weak-field limit, the applied field and the molecular structure are related. Although the effect of the applied field is important, the specific forms needed to control the NLO properties[11] were not generally recovered, similar to the findings of others.[15,16] However, the case of odd atom positive or negative ions exhibit the same BLA behavior as in ref 11. This result is a consequence of the symmetry of the problem, which is best understood by lifting the periodic boundary conditions and studying finite systems.

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Appendix

In this appendix we expand the determinant of a Hermitian tridiagonal matrix $\mathbf{M}$ in powers of its diagonal constituents. $\mathbf{M}^0$ is obtained from the original matrix by setting those diagonal elements to zero. For a general matrix

$$\mathbf{M} = \begin{pmatrix} \epsilon + \Delta_1 & t_{12} & 0 & ... & 0 \\ t_{21} & \epsilon + \Delta_2 & t_{23} & ... & \vdots \\ 0 & & \ddots & & 0 \\ \vdots & & & \epsilon + \Delta_{N-1} & t_{N,N-1} \\ 0 & ... & 0 & t_{N-1,N} & \mathrm{e} + \Delta_N \end{pmatrix} \qquad \text{(A1)}$$

$\mathbf{M}^0$ is obtained by setting $\Delta_j = 0 \; \forall \; j$.

The addition theorem of determinants[17] expresses a determinant whose constituents of a row or column consists of two terms as the sum of two determinants. The first contains the terms of the original determinant by excluding one term of each of the constituents, while the second contains those excluded terms. We apply this theorem to each of the columns. For example, from the decomposition of the first column of **M**

$$|\mathbf{M}| = \begin{vmatrix} \epsilon+\Delta_1 & t_{12} & 0 & \ldots & 0 \\ t_{21}+0 & \epsilon+\Delta_2 & t_{23} & \ldots & \vdots \\ 0+0 & & \ddots & & 0 \\ \vdots & & & \epsilon+\Delta_{N-1} & t_{N-1,N} \\ 0+0 & \ldots & 0 & t_{N,N-1} & \epsilon+\Delta_N \end{vmatrix} \tag{A2}$$

we obtain

$$\begin{vmatrix} \epsilon & t_{12} & \ldots & 0 \\ t_{21} & \epsilon+\Delta_2 & t_{23} & \ldots\vdots \\ 0 & & \ddots & \\ 0 & \ldots & t_{N,N-1} & \epsilon+\Delta_N \end{vmatrix} + \begin{vmatrix} \Delta_1 & t_{12} & \ldots & 0 \\ 0 & \epsilon+\Delta_2 & t_{23} & \ldots\vdots \\ 0 & & \ddots & \\ 0 & \ldots & t_{N,N-1} & \epsilon+\Delta_N \end{vmatrix} \tag{A3}$$

By applying the same procedure succesively and rearranging terms, we can obtain the following:

$$|\mathbf{M}| = |\mathbf{M}^0| + \sum_i \Delta_i |\mathbf{M}^0(i|i)| + \sum_i \sum_j \Delta_i \Delta_j |\mathbf{M}^0(ij|ij)| ... + \prod_i \Delta_i \tag{A4}$$

where $\mathbf{M}^0(i|j)$ is the cofactor of matrix $\mathbf{M}^0$, $\mathbf{M}^0(ij|ij)$ the matrix obtained by deletring rows i and j, as well as columns i and j, and so on.

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