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Bond length alternation in ground and HOMO →LUMO excited states in polyenes. Dynamic Stokes shift?

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Abstract. Complete-active-space self-consistent-field calculation of the reorganisation energy, λ, corresponding to the strongly allowed HOMO →LUMO transition in planar polyenes in the trans form (C_{2h} symmetry), gives $\lambda > 0.5$ eV. This large λ depends on the fact that the short and long bond lengths of the excited ^1B_u (or ^3B_u) state compared to the ^1A_g ground state are almost cancelled. The emission redshift (Stokes shift) in molecules with the same type of π system is quite small, however, which suggests that the Stokes shift may be dynamic, owing to the presence of another excited state at lower or about the same energy.

Keywords: Polyenes – Stokes shift – Electronic structure – Excitation – Complete-active-space self-consistent field

Introduction

Linear polyenes and other molecules with the same type of π conjugation are important as conducting polymers [1, 2] and play different roles in biology, for example, as visual pigments and as chromophores in photosynthetic systems [3]. Vitamin A is an oligomer containing ten carbon atoms in the conjugated system. Vitamin D is a molecule that has a hexatriene central part, which to a large extent determines its photochemistry. It is consequently of a great importance to know the basic features of the electronic structure of these systems along with the potential-energy surfaces (PESs) of the excited states.

In the case of vitamin D, the nonequilibration of excited rotamers (NEER) principle was formulated a long time ago [4]. It states that there is an enhanced barrier for rotation around a single bond and a lowered barrier for rotation around a double bond in the state where one electron has been excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The energy surface of a polyene for the ground state (1^1A_g) is simple and well known, with a minimum corresponding to alternant CC bond lengths. This may be simulated using the simple iterative Hückel model [5, 6, 7, 8] (see later). Symmetry labels for planar polyenes in the trans form (C_{2h} symmetry) will be used throughout in the following text.

The lowest ^1B_u state corresponds to lifting one electron from the HOMO to the LUMO, at least for smaller polyenes. This state will be called ^1B_u(HL) in the following text. Since the nature of this state appears to be approximately a simple one-electron excitation, the π bond orders, taking into account the new occupation numbers, should determine the new bond lengths. If the iterative Hückel model is used for the HL state, the result is that double bonds and single bonds are interchanged in the central part of the molecule. This is in perfect agreement with the assumptions behind the NEER principle and also suggests that torsion in the excited state takes place around bonds that are double bonds in the ground state. Thus, to the extent that Hückel bond orders are correct and can be used to predict bond lengths, the explanation for the NEER principle is simple and straightforward. The LUMO has one more node than the HOMO and consequently, if the HOMO is bonding between the two central carbon atoms, the LUMO is antibonding, and vice versa. Exciting one electron from the HOMO to the LUMO thus leads to a great change of the bond lengths.

The triplet state has been optimised for butadiene and hexatriene using a complete-active-space self-consistent field (CASSCF) with the 6-31G(d,p) basis set [9]. The results support the interchange of short and long bond lengths predicted by the Hückel model, but it is still questionable if the same alternation pattern holds for the

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corresponding singlet state, particularly since singlet states normally have larger contributions of electron correlation effects. The crude Hückel model does not make any distinction between singlet and triplet states.

The 2^1A_g state has about the same energy as the ^1B_u(HL) state for butadiene, hexatriene and octatetraene [10, 11] and is composed of HOMO−1 →LUMO and HOMO →LUMO + 1 single substitutions, and HOMO →LUMO double substitution. A state of this character cannot be simulated in the Hückel model, of course. There is some disagreement on the ordering between the 2^1A_g and the ^1B_u(HL) state. Serrano-Andrés et al. [12] investigated the spectrum of butadiene and hexatriene in the cis form. Ostojić and Domcke [13] investigated the PESs of the 2^1A_g and ^1B_u(HL) states in *trans*-butadiene and found that the energy order between these states may shift for certain geometries. Experimentally, for large polyenes (or correspondingly for carotenes), the 2^1A_g state is lower at the ground-state geometry in the absorption spectrum [14, 15].

Resonance Raman results for butadiene [16, 17] support the idea of a great bond length change in the excited state, since the CC symmetric stretch has very high intensity. Calculations on polyenes also support the great change of bond length, at least in the shorter polyenes [18].

Interchange of single and double bonds results in a great reorganisation energy, if the equilibrium geometries in both states are considered to be planar and of C_{2h} symmetry. The reorganisation energy is usually measurable as a Stokes shift (with corrections for zero-point vibrational energy and solvent shift). However, owing to the low emission quantum yield and since two excited states are involved, the Stokes shifts have been hard to measure and interpret. Where they have been obtained, the redshift of the maximum emission appears too small to correspond to an interchange of long bonds and short bonds [14, 15]. This hints that the Hückel model, even if it works well in predicting bond length changes at ionisation and electron attachment [7], performs less well for the HOMO →LUMO excited spin singlet state. Alternatively some kind of dynamic Stokes shift is measured, due to transition to the lower excited state. One purpose of the present work is therefore to try to calculate the reorganisation energy. Another purpose is to examine the iterative Hückel model (or the Su–Schrieffer–Heeger model). Since this model is extensively used, for example, in teaching and in the description of conducting polymers, it is important to investigate the behaviour of it in the case of smaller systems, when accurate models can be used as a comparison. In the present work we use a very reliable ab initio method: CASSCF [19, 20].

Calculation of reorganisation energy using the Hückel model

The reorganisation energy may be calculated approximately as [7]

$$\lambda = \frac{1}{2}\sum_{\mu\nu} k_{\mu\nu}\delta R^2_{\mu\nu}, \tag{1}$$

where $\{\delta R_{\mu\nu}\}$ are the bond length (or bond angle) changes between atoms μ and ν when the electronic state is changed, in the present case corresponding to a HOMO →LUMO transition. The summation extends over all CC bonds. We use $k = 750\ \mathrm{N\ m^{-1}}$ (0.4817 au), which corresponds to the vibrational wave number 1,456 $\mathrm{cm^{-1}}$. The CH bonds usually change insignificantly. Bond angle changes are also neglected.

The Hückel model is a tight-binding method that is applied only to the π electrons. There is thus only one "basis function" per carbon atom. The carbon atoms are usually considered as equivalent and the diagonal elements in the Hamiltonian matrix are set equal to α. The off-diagonal coupling matrix element between two carbon atoms is called β. The charge $P_{\mu\mu}$ on carbon atom μ and the bond order $P_{\mu\nu}$ (where μ and ν indicate bonded C atoms) depend on the occupation numbers n_i for MO ϕ_i according to

$$P_{\mu\nu} = \sum_i n_i c^*_{\mu i} c_{\nu i}, \tag{2}$$

where $\{c_{\mu i}\}$ are the coefficients of the π orbital ϕ_i on atom μ. The decrease of the conjugated bond length compared to a σ bond, assumed to be 1.534 Å, is proportional to $P_{\mu\nu}$. The proportionality factor is −0.2 Å, meaning that a full π bond ($P_{\mu\nu} = 1$) decreases the bond length by 0.2 Å. The bond length is then given by

$$R_{\mu\nu} = -0.2P_{\mu\nu} + 1.534\ (\text{Å}). \tag{3}$$

It is reasonable to let β depend on the bond length $R_{\mu\nu}$. An empirical equation is used [6]:

$$\beta = \beta_0 \exp\left[-(R - R_0)/0.3106\right]. \tag{4}$$

In an iterative scheme the bond lengths are calculated according to Eq. (3) and the β values for individual bonds according to Eq. (4). Bond length alternation appears, even in a cyclic or infinite polyene where all carbon atoms are equivalent, except for a few cases where the number of carbon atoms, N, is small and is of the form $N = 4n + 2$ [$N = 6$ (benzene), 10, and possibly 14] [8]. For sufficiently long polyenes with an even number of carbon atoms the difference in bond length converges to 0.08 Å as $N \to \infty$. There is a gap in the orbital energy spectrum as required by experiments. If $|\beta_0|$ is given the reasonable value of 3 eV, the band gap is 1.6 eV. The predictions of the CC bond length by this theory are in qualitative agreement with accurate abinitio results and experimental bond length data [7, 8].

In the HOMO →LUMO excited state the occupation numbers are changed in Eq. (2) and iterations are carried out. The difference in bond length between the ground state and the HOMO →LUMO state is used to calculate reorganisation energies by Eq. (1). The result is given in Table 1.

Calculation of reorganisation energy using the CASSCF model

To obtain the reorganisation energy, λ, one may use the bond lengths calculated with Eq. (1). A more accurate way is to perform single-point calculations using optimised structures. The geometry is first optimised for the $1A_g$ (ground) state. The total energies are E_0 for the $1A_g$ state and E_1^* for the B_u(HL) state (Fig. 1). The asterisk indicates that the energy is calculated for a geometry different from the equilibrium geometry. Subsequently the geometry is optimised for the B_u(HL) state. The total energies are E_0^* for the ground state and E_1 for the B_u(HL) state. The reorganisation energy is obtained as (Fig. 1)

$$\lambda = E_1^* - E_1 + E_0^* - E_0. \tag{5}$$

We performed the previously mentioned geometry optimisations on the molecules butadiene, hexatriene, octatetraene and decapentaene in the planar trans form. The geometries were optimised for both the ground state (1^1A_g) and the excited state corresponding to a HOMO →LUMO transition [^1B_u(HL)]. The symmetry properties of the molecules correspond to the C_{2h} point group. The method used was CASSCF [19, 20] as implemented in the MOLCAS 5.0 program [21]. The choice of basis set was inspired by the extensive investigation of the spectra of butadiene and hexatriene by Serrano-Andrés et al. [12]. The large atomic natural orbital basis set [22] with 1s, 2s, 2p, 3s, 3p, 4s, 3d and 4p functions on the carbon atoms and 1s, 2s and 2p functions on the hydrogen atoms was used. In Ref. [12] diffuse functions were used since the aim was to describe Rydberg as well as valence excited states. We chose not to include diffuse functions for reasons of saving calculation time and because Rydberg states are not of interest in this work. The active spaces were chosen to consist of all valence π orbitals i.e. four electrons in four orbitals for butadiene, six electrons in six orbitals for hexatriene, eight electrons in eight orbitals for octatetraene and, finally, ten electrons in ten orbitals for decapentaene.

Table 1. Reorganisation energy, λ, for excitation to the ^1B state, corresponding to HOMO →LUMO substitution, for a linear polyene with N carbon atoms. *Middle column*: simulated using the Hückel model and Eq. (1). *Right column*: calculated using the complete-active-space self-consistent-field (*CASSCF*) method and Eq. (5).The large atomic natural orbital basis set was used with 1s, 2s, 2p, 3s, 3p,4s, 3d, 4p functions on carbon and 1s, 2s, 2p functions on hydrogen

N	λ (eV) (Eq. 1)	λ (eV) (Eq. 5)
4	0.703	0.608, 0.515[a]
6	0.663	0.586[a]
8	0.666	0.569[a]
10	0.689	0.571[a]

[a] State-averaged CASSCF method used for the calculation of E_1^* and E_1 in Eq. (5)

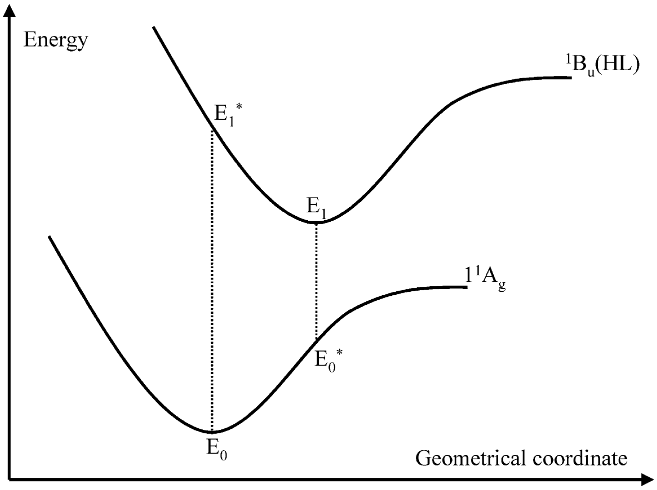

Fig. 1. Graphical explanation of reorganisation energy (Eq. 5)

For hexatriene, octatetraene and decapentaene, problems occur when the excited B_u(HL) state is calculated. It turns out that with the basis set and active spaces mentioned, the state dominated by a Slater determinant with one electron excited from HOMO to LUMO is not the lowest state of B_u symmetry in either of these molecules. For hexatriene and octatetraene there is a state below with diffuse, multiconfigurational character, also found for *cis*-hexatriene by Serrano-Andrés et al. [12] and Woywod et al [23]. In our previous work [24] the same problem occurred. Woywod et al. pointed out that if dynamic correlation is included in the calculations by adding second-order perturbation theory (CASPT2), this problem disappears for the ground-state equilibrium geometry for hexatriene and the lowest state of B_u symmetry is B_u(HL) [23].

Since the states of B_u symmetry are close in energy, the calculations are difficult owing to root flipping. To avoid this problem the state-average CASSCF (SA-CASSCF) procedure was used for the B_u(HL) state. In this method the CASSCF energy functional is not optimised for one specific state, but for a number of states, defined by the user, i.e. the orbitals are not optimal for the B_u(HL) state. The bond length changes occurring when the geometry is optimised for this state may be less accurate for this reason. For hexatriene and octatetraene the two lowest states of B_u symmetry were used in the SA-CASSCF calculations. Since the density of states is increased as the polyene chain length is increased, the HOMO →LUMO state appears sometimes as the third state during geometry optimisation for decapentaene and therefore the three lowest states were used for this molecule. Care was taken that the correct state was geometry-optimised.

For butadiene, the CASSCF and SA-CASSCF methods were both employed to test if the two methods give consistent reorganisation energies. The difference is a tolerable 0.093 eV (Tables 1, 2).

To summarise, the ground states (E_0* and E_0) were calculated for all four molecules using the ordinary CASSCF procedure. For all molecules E_1* and E_1 were calculated using SA-CASSCF. For the three smallest molecules the two lowest states of B_u symmetry and for decapentaene the three lowest states were included in the SA-CASSCF calculations. For butadiene E_1* and E_1 were also calculated with the ordinary CASSCF method.

Results and discussion

For butadiene, hexatriene, octatetraene and decapentaene the bond lengths of the ground states were calculated to be approximately the same by the CASSCF method as in the Hückel simulation. In Table 1 we find that λ is calculated to be about the same by the CASSCF method (around 0.6 eV) as in the Hückel simulation model (around 0.7 eV). In Table 2 we find that the differences between bond lengths in the 1^1A_g and ^1B_u(HL) states are smaller using the CASSCF method than the Hückel simulation. However, if the comparison is made to CASSCF calculations for the lowest triplet state of B_u symmetry, corresponding to a HOMO →LUMO transition, ^3B_u(HL), [9, 25], the latter method gives larger bond length changes, even larger than with the Hückel model. In the Hückel calculations no distinction between triplets and singlets is made and hence the same Hückel results apply in the singlet and triplet cases.

For butadiene the central bond increases while the other two bonds decrease, as predicted from bond orders (Table 2). The bond length changes from the ground state to the excited state are less in the ab initio calculation and hence the reorganisation energy is less. However, if Eq. (1) is used to obtain the reorganisation energy from the calculated bond lengths, the ab initio results are even smaller, or half of the Hückel results. For hexatriene in the excited state the long bond, usually indicated as a single bond, decreases by 0.06 Å in the CASSCF calculation compared to 0.07 Å in the Hückel calculation, while the central short bond increases by 0.06 Å in the CASSCF calculation and by 0.11 Å in the Hückel calculation. Octatetraene and decapentaene follow the same pattern: ground-state double bonds are stretched and ground-state single bonds are contracted.

The CASSCF ^1B_u(HL) state is composed of 0.79% HOMO →LUMO substitution for decapentaene, 85% for octatetraene, 89% for hexatriene and 99% for butadiene. The reason for the discrepancy between Hückel and ab initio results is not too surprising, considering the extremely simple character of the Hückel wave function, for example, that it corresponds to a single Slater determinant.

How is it possible that a trivially simple model such as the iterated Hückel model [5, 6, 7, 8] can simulate accurate ab initio calculations reasonably well (at least for the triplet state)? Since the ^1B_u(HL) state rather closely corresponds to a HOMO →LUMO excitation and the wave function thus approximately is a one-determinant wave function for shorter polyenes, the reason for the geometry changes may easily be tracked from the orbital structure. The nodal structure of the π MOs is the traditional one with an increasing number of nodal surfaces, which can easily explain bond lengths. Removing one electron from the HOMO leads to less bonding between double-bonded atoms and greater bonding between single-bonded atoms. The positive ion has about equal bond lengths in the central part of the molecule [7]. The LUMO, on the other hand, is antibonding between double-bonded atoms and bonding between single-bonded atoms, at least in the central part of the molecule. Adding one electron to the LUMO thus leads to the same result as removing one from the HOMO, i.e. about equal bonds in the central part of the molecule [7]. In the excitation to the ^1B_u(HL) state, one electron is removed from the HOMO and is added to the LUMO, and hence the effect is twice as large as for ionisation or electron attachment. The short bonds become long bonds and vice versa.

This simple description of bond length change has some pedagogical significance. In teaching theoretical chemistry to students who are becoming acquainted with wave functions for the first time, it is necessary to use models as simple as the Hückel model. That this model may be used to predict geometries after ionisation or electron attachment processes in a physically reasonable way is in a sense very satisfactory [7].

Table 2. Calculated bond lengths, R (Å), in the 1^1A_g, ^1B_u(HL) and ^3B_u(HL) states for linear polyenes with N carbon atoms (end bonds given first)

N	Hückel		CASSCF		
	Ground state	HOMO →LUMO substitution	1^1A_g	^1B_u(HL)	^3B_u(HL)
4	1.344, 1.471	1.449, 1.381	1.343, 1.462	1.401[a], 1.378[a] 1.403, 1.393	1.458[b], 1.361[b]
6	1.346, 1.456 1.356	1.406, 1.394 1.461	1.344, 1.459 1.348	1.385, 1.400 1.406	1.414[b], 1.375[b] 1.471[b]
8	1.347, 1.464 1.359, 1.459	1.385, 1.411 1.443, 1.381	1.344, 1.458 1.349, 1.454	1.372, 1.410 1.397, 1.393	1.390[c], 1.394[c] 1.453[c], 1.360[c]
10	1.347, 1.463, 1.360, 1.456 1.363	1.373, 1.424 1.425, 1.386 1.440	1.344, 1.457 1.350, 1.453 1.351	1.365, 1.419 1.390, 1.397 1.395	

[a] OrdinaryCASSCF without state averaging
[b] Taken from Ref. [9]
[c] Taken from Ref. [25]

A question that may be raised is whether the predicted result is physically realistic in the case of an extended system. Using the iterative Hückel method described earlier, one may extend the calculation to a very large number of carbon atoms. The result is that the double bonds and single bonds are swapped over a large number of carbon atoms (50 in a calculation with 100 carbon atoms). However, when increasing the number of atoms of the polyene, the Hückel approximation will probably become more and more physically irrelevant. As mentioned earlier, the orbital energy differences decrease as the chain length is increased, which causes more and more states to be close in energy. This is seen when the weight of the Slater determinant corresponding to a HOMO → LUMO in the ^1B_u(HL) wave function is examined. It decreases as the chain length is increased (see earlier). In other words, correlation effects are enhanced for longer polyenes. Since the Hückel approximation corresponds to a single Slater determinant the results cannot be trusted when the polyene chain is very long.

A comparison between the calculated λ and the experimental Stokes shift is of interest. Unfortunately no fluorescence spectra appear to have been published for polyenes shorter than tetradecaheptaene and decatetraene (an octatetraene analogue) [14, 26]. The latter spectra show the highest intensity on the first or second vibrational level at absorption and emission, indicating a small Stokes shift. The processes on the excited PES have been studied both experimentally and theoretically [26, 27, 28, 29, 30, 31, 32]. Crawczyk et al. [32] obtained very good agreement with the measured absorption spectrum. The ^1B_u(HL) state interacts electronically via asymmetric modes with the 2^1A_g state immediately after excitation. The PES of the new, symmetry-broken, upper state may form a funnel rather near the geometry of the ground state. Emission to the ground state can take place with a geometry close to the ground-state equilibrium geometry and the planar ^1B_u(HL) state equilibrium geometry may never be reached.

Conclusion

The bond reorganisation energy after excitation to the ^1B_u(HL) state in a polyene is large and of the order of 0.5 eV or more. The reason for this is the great change in bond lengths at excitation. This bond length change is greatest for the triplet states, where short and long bonds are swapped, at least in the central part of the molecules. The latter results are consistent with the iterated Hückel results. For the singlet states the bond length alternation almost disappears, probably owing to correlation effects.

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