The Response of Electronic And Energetic Properties of Two Types of The Sp-hybridised Carbon-Carbon Bonds To An External Uniform Electric Field

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Research Article

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Abstract

The susceptibility of electronic and energetic properties of two sets of molecules to perturbation in a uniform electric field was investigated. The molecules of one set were (10)cumulenes terminated with two functional groups, R_1 and R_2 ; those of the second set were (10)polyyenes substituted with the same R_1 and R_2 groups. The cumulene and polyyne molecules had similar lengths of the system of conjugated bonds between the two most extreme carbon atoms. Dipole moments and polarizabilities of the molecules were used as determinants of the overall charge transfer between polar groups and their modifications due to the application of an external electric field. The field was directed along the main (longest) axis of the molecules from the negative to the positive pole. Comparison of the polarizability values revealed that they were higher in the (10)cumulenes than in the (10)polyyenes. Parabolic dependence of the molecular energy as function of field strength can be interpreted in terms of the response of electron density to an electric field.

Introduction

Electric fields affect chemical reactions as the field can significantly alter the potential energy curves near the transition state region governing chemical reactions [1] and consequently, influence course and rate constants of the reactions. This way fields may also impact the biological properties of cells and their components. Impact of the external electric fields on diatomic molecules: energies, geometries, and vibrational Stark shifts is described by Sowlati-Hashjin and Matta [1]. These effects of the electric field were investigated both theoretically and experimentally. A comprehensive and informative review of structure and reactivity control has been written by Shaik et al. [2]. Most effects can be comprehended as field-augmented transition state stabilisation by ionic structures [2]. The interaction of molecules with external fields may result in the breaking and making of chemical bonds.

Upon variation of electric field and polarity, it is possible to stabilise different tautomeric forms of a molecule [3]. An electric field may also perturb molecular vibrations; the largest change in the IR spectrum induced by the field is a linear frequency shift [4]. There are many other reports describing the impact of electric field on the properties and reactivity of molecules [5–10].

This study is a continuation of the previous work [5] where the susceptibility of two other sets of molecules to perturbation in a uniform electric field was investigated. The molecules of one set were deca-1,3,5,7-pentaenes terminated with two functional groups, R_1 and R_2 ; those of the second set were 4- R_1 -4'- R_2 -p-diphenylbenzenes, with R_1 and R_2 being the same as in the pentanes set. Comparison of the effect of the charge relocations in both series of the conjugated molecules revealed that the charge transfer imposed by the electric field was more efficient in the pentanes than in the aromatic compounds. From the point of view of this study, the most interesting papers are those dealing with molecules containing chains of carbon atoms [11–13]. Action of an electric field on atoms or molecules [14–18] can be measured and visualised with polarizability, resulting from the interaction of atoms or molecules with the field of their interaction or an atom or molecule in electric field. This computational study aims at

gaining insight into the effect of external fields in two groups of molecules: polyynes and cumulenes with the same substituent pairs (Fig. 1). The examined cumulenes belong to class of even cumulenes, i.e. with an even number of cumulated double bonds [11].

Dipole moments were used as a measure of the overall charge transfer within the molecules, as in the case of deca-1,3,5,7-pentaenes and 4-R₁-4'-R₂-p-diphenylbenzenes groups. Thus, the links (*linkers*) connecting substituents were chains of ten *sp*-hybridised carbon atoms. In molecules of one type, known as cumulenes, the carbon atoms are connected with double bonds, whereas in molecules of the second type, named polyynes, there are alternating single and triple bonds. Due to polar substituents, all molecules of both types are polarised and their energies depend on the applied field intensity. The polarizability values were calculated as slopes of the plots:

$$dE_n/dF \text{ vs } F, (1)$$

where E_n stands for the energy of a molecule in an electric field and F stands for the intensity of the applied field.

Polarizability is believed to play an important role in intermolecular interactions of heterogenous media such as protein-ligand binding. The methods of calculation of molecular dipole moments and polarizabilities was benchmarked [18].

Electron transmission through molecules and molecular interfaces has been a subject of intensive research due to a recent interest in electron transfer phenomena underlying the operation of the scanning-tunnelling microscope on one hand and in the transmission properties of molecular bridges between conducting leads on the other [19]. Most electric field effects on molecular structures and reactions can be comprehended as the field-induced stabilisation of ionic structures.

Calculation

Molecular geometries were optimised with and without external fields. All calculations were conducted using the Gaussian 09 program [20]. The calculations were conducted using Lee-Yang-Parr correlation functional {B3LYP} [21]. The 6-31 + G{d} basis set with the polarised and diffusion functions was employed. The values of the electric field strength used in our calculation were taken from the interval - 0.015 to 0.015 a.u. (-7.71×10^9 V/m to $+7.71 \times 10^9$ V/m). The fields were applied along the x-axis of the coordinate system. The C-C chains were approximately parallel to the x-axis of the coordinate system therefore all fields in this study have the same direction as the x-axis along which they are aligned (Fig. 1).

The axes were oriented so that the dipole moments of all molecules without any applied electric field were positive – that is, the dipole moments originate at the negative pole and point to the positive pole. Plots of the calculated energies against the field intensity (F) are shown for (10)cumulenes in Fig. 2 and for (10) polyynes in Fig. 3 with the NO₂ and CN substituents. Molecular polarizabilities were eventually

obtained as slope values of the numerical derivatives of the calculated energies with respect to the applied field (Figs. 2b and 3b). Evaluation of a range of density functional theory (DFT) methods and basis sets used to calculations using Hartree-Fock theory is provided by Hickey and Rowley [18].

Results And Discussion

3.1. Comparison of polarizabilities of the cumulenes and polyynes chains connecting the same substituents.

Energies of the eight investigated systems (four cumulenes and four polyynes with different R_1 and R_2 substituents) were plotted as functions of the intensities of the applied field. These functions were represented as practically perfect parabolas, with coefficients of determination in the 0.999–1.000 limits. Two examples of this plot are shown in Fig. 2a for (10)cumulene and in Fig. 3a for (10)polyyne bearing the same substituents, NO_2 and CN . The functions of energy (E_n) against the electric field strength (F) may be expressed by following quadratic Eq. (2), which is correct in the case where the fields that are co-linear with the molecular axis were applied and higher terms in F may be neglected [22]. Figures 2a and 3a display energies of cumulenes and polyynes as functions of the strength of the electric field:

$$E_n = E_o + \mu_o F - \frac{1}{2} a F^2 \quad (2)$$

In Eq. (2), μ_o is a dipole moment of a neutral molecule without the applied field and a denotes molecular polarizability, a value which is a measure of the energy increment due to the dislocation of electron density within the molecule under the action of the electric field.

Based on Eq. (2), one may determine the dipole moment of the molecule without the field (μ_o) and in the field ($\mu(F)$) using the following equations:

$$dE_n/dF = \mu_o - aF \quad (3)$$

$$\mu(F) = \mu_o + aF \quad (4)$$

In a case where Eq. (3) is valid, the plot of dE_n/dF against F should be a straight line with a slope equal to a and an intercept equal to the field-free dipole moment μ_o . Such plots are shown in Figs. 2b and 3b, for the cumulene and polyyne molecules with NO_2 and CN substituents. The same calculations were performed for another cumulenes and polyynes with different substituents R_1 and R_2 such as NO_2 , NH_2 , OH , CN . It should be emphasised that the coefficients of determination of dE_n/dF against F for all eight molecules are 1 up to four decimals. Dipole moments of the molecules in the electric field directed along the x-axis, as shown in Fig. 1, were determined according to Eq. (4). As can be seen, dipole moments in the electric field directed along the x-axis of the molecules are larger for substituted cumulenes (Tables 1) than for polyynes (Table 2).

Table 1
Dipole moments of the (10)cumulenes with two substituents, R_1 and R_2

F (atomic units)	$R_1 = \text{NO}_2$ $R_2 = \text{CN}$	$R_1 = \text{NO}_2$ $R_2 = \text{NH}_2$	$R_1 = \text{NO}_2$ $R_2 = \text{OH}$	$R_1 = \text{OH}$ $R_2 = \text{NH}_2$
-0.015	17.5	23.9	21.1	17.0
0	1.01	6.40	4.92	1.79
0.015	-15.6	-11.1	-11.3	-13.4

Table 2
Dipole moments of the (10)polyyenes with two substituents, R_1 and R_2

F (atomic units)	$R_1 = \text{NO}_2$ $R_2 = \text{CN}$	$R_1 = \text{NO}_2$ $R_2 = \text{NH}_2$	$R_1 = \text{NO}_2$ $R_2 = \text{OH}$	$R_1 = \text{OH}$ $R_2 = \text{NH}_2$
-0.015	11.81	20.66	18.24	14.3
0	0.34	6.11	4.72	1.24
0.015	-11.13	-8.44	-8.81	-16.74

Electric dipole moment atomic unit is $e a_0$ where e – is electron charge and a_0 – Bohr radius. The electric dipole moment atomic unit equals $8.478 \times 10^{-30} \text{ C}\cdot\text{m}$ or 2.542 D (debye).

Polarizabilities of the substituted cumulenes and polyyenes, obtained from the derivative of the electronic energy (E_n) with respect to F , are given in Table 3. The data show that polarizability values of cumulenes are 7–25% higher than those of polyyenes.

Table 3
Polarizability of substituted cumulenes and polyyenes in atomic units

	$R_1 = \text{NO}_2$ $R_2 = \text{CN}$	$R_1 = \text{NO}_2$ $R_2 = \text{NH}_2$	$R_1 = \text{NO}_2$ $R_2 = \text{OH}$	$R_1 = \text{OH}$ $R_2 = \text{NH}_2$
(10)cumulene- R_1R_2	-1102	-1167	-1122	-1011
(10)polyyne- R_1R_2	-975	-970	-901	-949

Polarizability atomic unit is $e^2 a_0^2 / E_h$, where e – is electron charge, a_0 – Bohr radius, and E_h – hartree. The polarizability atomic unit equals $1.649 \times 10^{-41} \text{ C}^2\text{m}^2/\text{J}$.

3.2. Comparison of two types of the *sp*-hybridised carbon-carbon double bonds.

Figure 1 shows that the carbon atoms are linked by double bonds in cumulenes, whereas in polyynes there are alternating single and triple bonds. To verify this structure, we compared bond length values for two series of molecules with the same functional groups without the applied electric field and with the field of intensities + 0.01 and – 0.01 a.u. The data is shown in Table 4.

Table 4
Comparison of mean bond lengths of the C-C bonds in 10-cumulene-NO₂CN and 10-polyyne-NO₂CN and their standard deviations

	(10)cumulene-R ₁ R ₂			(10)polyyne-R ₁ R ₂		
Field, a.u.	0	0.01	-0.01	0	0.01	-0.01
Mean value of bond length	1.29	1.29	1.30	1.28	1.28	1.28
SD of bond length	0.024	0.024	0.029	0.050	0.050	0.045

Data in Table 4 is evidence that the mean bond lengths of the link between two functional groups are nearly the same for the both types of the linker and do not change when the electric field (of the strength of + 0.01 and – 0.01 a.u.) is applied. These values (1.29 and 1.28 Å) can be compared with values of lengths of the single, double, and triple bonds calculated for the CH₃-CH₃, CH₂ = CH₂, and CH ≡ CH at the same calculation level (B3LYP/6–31 + G*). The values were 1.53 (1.532), 1.34 (1.335), and 1.21 (1.2075) Å, respectively. The comparison showed that the bonds in both types of molecules can be represented as double bonds with a small addition of triple bond. Cumulenes do not exhibit a substantial bond length alternation as compared with that of polyynes. Standard deviations of bond length for polyyne-NO₂CN (0.05Å) are twice as large as that for cumulene-NO₂CN (0.02–0.03 Å).

Conclusions

The reaction of cumulene and polyyne molecules with similar length of conjugation to electric field was compared. We report that polarizability of cumulenes is 7–25% higher than that of polyynes. Standard deviation of carbon-carbon bond length is twice as large in the group of polyynes as in the group of cumulenes. It turned out that the communication between two electroactive moieties (ending groups with varying degrees of polarity) connected to two different chains of the *sp* carbon atoms is stronger in the group of cumulenes than in the group of polyynes.

Declarations

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Figures

The electric field

Figure 1

Chemical structures of compared polyynes and cumulenes

Figure 2

(a) Energy (E_n) of the (10)cumulene molecule with the NO₂ and CN substituents as a function of the applied electric field (F) parallel to the molecular axis; (b) Plot of the derivative of energy of the (10)cumulene molecule with the NO₂ and CN substituents with respect to F

Figure 3

(a) Plot of E_n of the (10)polyyne molecule with the NO₂ and CN substituents as a function of F in atomic units; (b) Plot of the derivative of energy of the (10)polyyne molecule with the NO₂ and CN substituents with respect to F