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UV-vis absorption spectra of 1,4-dialkoxy-2,5-bis [2-(thien-2-yl)ethenyl]benzenes

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ABSTRACT

Complex theoretical and experimental studies and quantum-chemical calculations were applied to study the UV-vis spectroscopic features of the novel compounds: three stereoisomers of 1,4-diethoxy-2,5bis[2-(5-methylthien-2-yl)ethenyl]benzene (**A**–**C**) and *E*,*E* isomer of 1,4-diisopropoxy-2,5-bis[2-(thien-2-yl)ethenyl]benzene (**D**). These structures are the derivatives of 2,5-bis[2-(thien-2-yl)ethenyl]benzene, and belong to a group of thienyl–PPV family that are able to polymerize due to the presence of π conjugated bonding system. It was established that such compounds during electropolymerization are strongly dependent on their stereochemistry and on the eventual presence of substituents in α -positions of the tiophene ring. We have obtained a good agreement between the theoretically simulated optical within a framework of TDDFT approach and experimentally measured data. Influence of PMMA polymer matrices on the UV–vis spectra is explored. It is shown that a red wavelength spectral shift is observed only for **D** compounds and agreement between calculated and experimental spectral data is sufficiently good. This may indicate on different influence of local polymer matrix field on the spectral behaviors of the chromophores with different stereochemistry.

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SPECTROCHIMICA

1. Introduction

The research of benzene derivatives is of great importance due to possible promising nonlinear optical properties. One of the principal directions of search and design of novel nonlinear optical materials consists in finding of the practical ways to enhance their nonlinear optical susceptibilities [1]. Particularly it is crucial during the search of new transparent materials possessing very low losses and large nonlinear optical response. Particular interest presents chemical modifications of the π -conjugated chromophore by appropriate substitution by other chemical complexes.

At the same time the organic conjugated materials are of great interest for application as active components in photovoltaic devices [2]. Advantages of using organic materials in these devices are: low cost, facile processing, thin size, flexibility of properties and shape [3]; however one of the drawbacks of organic materials is their low chemical stability. The knowledge of UV–vis spectroscopical features plays here a principal role.

In the present work we study UV-vis spectral features of three stereoisomers: 1,4-diethoxy-2,5-bis[2-(5-methylthien-2yl)ethenyl]benzene (A-C) and E,E isomer of 1,4-diisopropoxy-2,5-bis[2-(thien-2-yl)ethenyl]benzene (D) belonging to so called thienyl PPV derivatives. They were synthesized in the course of our research on synthesis and electropolymerization of that type of compounds. A behavior of that type of compounds during electropolymerization strongly depends on their stereochemistry [5] and on the eventual presence of substituents in α -positions of the tiophene ring. When the α -positions are free the polymerization occurs readily to afford linear polymers; when the α -positions are blocked by, e.g. alkyl groups like in A-C, a mechanism of the reaction changes and at higher potentials the double bonds are involved in electropolymerization [6]. The α -blocked isomers are also more stable while irradiation. A type of alkoxy groups in benzene core is of secondary importance for the process; it influences the stability of stereoisomers, solubility of monomers and polymers.

In this work spectroscopic and theoretical calculations are applied to study the properties of the molecules as shown in Fig. 1. These structures are derivatives of 2,5-bis[2-(thien-2-yl)ethenyl] benzene, thus belonging to a group of thienyl–PPV family that are able to polymerize due to the presence of conjugated bonding sys-

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Fig. 1. Chemical formula of studied compounds1,4-dialkoxy-2,5-bis[2-(thien-2-yl)ethenyl]benzenes (A-D), where (1) A; (2) B; (3) C; (4) D.

tem [4–8]. These types of molecules, which are in fact short-chain models of the corresponding polymers, have properties similar to their high molecular weight analogs [9].

2. Experimental

General scheme of 1,4-dialkoxy-2,5-bis[2-(thien-2-yl) ethenyl]benzenes synthesis is presented below:

Boetius HMK apparatus. NMR spectra were taken in CDCl₃ with TMS as an internal reference by Varian XL-300 at 300 MHz for ¹H and at 75.5 MHz for ¹³C. EA results were obtained using Perkin-Elmer CHN automatic analyzer. For the separation of stereoisomers the Waters chromatograph with Prep. Nova-Pak[®] column HR C18 (19 mm × 300 mm) was applied. Methanol (5 ml/min) was used as the eluent at 520 psi of the pressure and at the temperature 26 °C; detection UV at 220 nm.



All solvents have been dried and distilled before use. Other commercial substances and reagents were applied without purification. Melting points (not corrected) were determined on

MS spectra were obtained from HPLC–MS Integrity Systems with Termabeam Mass Detector (EI, 70 eV); samples (in methanol

Table 1

Theoretically calculated and experimentally measured principal spectral maxima positions for the investigated chromophore.

Chromophore	Experimental peak (nm)	Theoretical peak (nm) ADF	Experimental spectral peak positions in nm shifted in PMMA matrices
A	$A_1 = 400$ $A_2 = 495$	$A'_1 = 355$ $A'_2 = 490$	$A'_1 = 362$ $A'_2 = 494$
В	$B_1 = 225$ $B_2 = 350$ $B_3 = 400$ $B_4 = 445$	$B'_1 = 235$ $B'_2 = 287$ $B'_3 = 350$ $B'_4 = 440$	$\begin{array}{l} B_1' = 228 \\ B_2' = 282 \\ B_3' = 353 \\ B_4' = 439 \end{array}$
С	$C_1 = 240$ $C_2 = 270$ $C_3 = 348$ $C_4 = 470$	$C'_1 = 230$ $C'_2 = 285$ $C'_3 = 355$ $C'_4 = 500$	$\begin{array}{l} C_1' = 237 \\ C_2' = 278 \\ C_3' = 352 \\ C_4' = 489 \end{array}$
D	$D_1 = 280$ $D_2 = 370$ $D_3 = 400$ $D'_4 = 540$	$D'_1 = 230$ $D'_2 = 275$ $D'_3 = 340$ $D'_4 = 520$	$\begin{array}{l} D_1'' = 280 \\ D_2'' = 390 \\ D_3'' = 418 \\ D_4'' = 562 \end{array}$

solutions) were introduced to the spectrometer using direct inlet. X-ray diffraction data were collected on KUMA KM4 four-circle diffractometer at 295 K. Cell parameters, reflection collection and their reductions were done using KUMA KM4 software [10]. The structures were determined by means of direct methods and refined by the full-matrix least squares technique [11].

The structure of (E,E)-1,4-diisopropoxy-2,5-bis[2-(thien-2-yl)ethenyl]benzene in the crystalline state was additionally monitored by X-ray measurements (CCDC no. 27369510).

Table 1 contains more important data concerning crystal, diffractometer, measurement conditions and refinement. The tiophene rings in the crystal are disordered over two orientations like in other similar compounds [12] (Fig. 2).

3. Results and discussion

All the quantum-chemical computations were done using Amsterdam Density Functional package (ADF) and HyperChem package. The first step we found was the geometry optimization by molecular mechanics force filed (MM+), which is the most general and frequently used method for molecular mechanics calculations developed principally for organic molecules. The geometry optimization and the calculation of optical spectra for separated

Fig. 2. Molecular structure of (E,E)-1,4-diisopropoxy-2,5-bis[2-(thien-2-yl)ethenyl]benzene showing 50% probability displacement ellipsoids obtained by ORTEP 3. A dominant conformation (82% probability) in the crystal is indicated by numbered atom symbols without the letter "b".

molecules **1–4** were accomplished by using a semi-empirical quantum-chemical method: AM1. The geometry relaxation's optimization performed by the Steepest Descent algorithm after the molecular geometry optimization. The values of the total energy minima were varied at around 4 eV/atom.

Simultaneously we have used the ADF program for molecular structure optimization. We obtained the optimization geometry with basis set: DZ (double zeta) because we find the molecular geometry for molecules with the lowest energy. The basis set chosen will apply to all atoms in our molecules. The ADF program uses Slater-type orbitals. There are a number of basis sets that can be freely downloaded. These basis sets are optimized for use in the zeroth-order regular approximated (ZORA) relativistic equation, which is an excellent approximation to the fully relativistic Dirac equation, especially in the valence region, which is important in quantum-chemical calculations. ZORA STO basis sets that can be downloaded freely: DZ fc (double-zeta frozen core). DZ ae (double-zeta all electron), TZP fc (triple-zeta frozen core 1 polarization function), TZP ae (triple-zeta all electron 1 polarization function), TZ2P fc (triple-zeta frozen core 2 polarization functions), TZ2P ae (triple-zeta all electron 2 polarization functions), and QZ4P ae (quadruple-zeta all electron 4 polarization functions). Seven different types of Slater-type basis sets for the elements H (Z=1) up to E118 (Z = 118), ranging from a double-zeta valence quality up to a quadruple-zeta valence quality, are tested in their performance in neutral atomic and diatomic oxide calculations. The exponents of the Slater-type functions are optimized for use in (scalar relativistic) ZORA equations.

The *double-zeta basis set* is very convenient because it allows us to treat each orbital separately when we conduct the Hartree–Fock calculation. These descriptions are meant to give an indication of the quality. This gives us a more accurate representation of each orbital. In order to do this, each atomic orbital is expressed as the sum of two Slater-type orbitals (STOs). The two equations are the same except for the value of ξ (zeta) [13]. The zeta value accounts for how diffuse (large) the orbital is. Then the two STOs are added in some proportion.

In this case, each STO represents a different sized orbital because the zetas are different. The 'd' accounts for the percentage of the second STO to add in. The linear combination then gives us the atomic orbital. Since each of the two equations is the same, the symmetry remains constant. After we used the Single Point added Excitations (Allowed only), this method determined the SCF solution and properties running the current geometry.

Fig. 3 presents the principal structures for the four studied molecules **1–4** with highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). In all the figures the HOMO orbital is indicated as full areas and the LUMO is marked as lined areas. The hydrogen atoms was drawn as white spheres and the carbon atoms as black spheres, each others atoms are noted by red (oxygen) and yellow (sulfur).

The UV–vis spectra were recorded by Ocean Optics HR4000CG-UV–NIR spectrometers (wavelength range 200–1100 nm, spectral resolution 1 nm FWHM (full width at half maximum), 3648element linear silicon CCD array) and the Ocean Optics DT-MINI-2-GS light source. The power output of light source was 3.8 W for deuterium lamp (200–410 nm) and 1.2 W for tungsten halogen lamp (360–2000 nm). Absorption was calculated automatically by the software by the following equation:

$$A_{\lambda} = -\log_{10}\left[\frac{S_{\lambda} - D_{\lambda}}{R_{\lambda} - D_{\lambda}}\right]$$

The light source, sample chamber and the spectrometer were connected together by the 400 μm diameter fiber optics with collimating lenses.



Fig. 3. 3D visualization of examined molecules. Plain surfaces, HOMO levels and transparent surfaces, LUMO levels.

When this equation is evaluated for each pixel of the detector, the absorbance spectrum is produced, where *S* is the sample intensity at wavelength λ , *D* is the dark intensity at wavelength λ , and *R* is the reference intensity at wavelength λ .

The calculated optical spectra were consequently performed for isolated chromophore molecule as well as for the chromophore incorporated into the PMMA polymer matrices. However, we will also give theoretically simulated spectra obtained within a framework of time-dependent DFT method (TDDFT) using ADF package. We have found a good agreement with the experimental spectra taking into account only the singly excited configuration interactions. The criteria regarding the excitation energies were chosen to include seven occupied and seven unoccupied orbital for both methods. Our quantum-chemical calculations have been performed for isolated molecules in vacuum. The experimental absorption spectra in the THF solution were determined by the Gaussian approximation, theoretical absorption spectra were calculated using SWizard program [14]. Absorption profiles were calculated using Gaussian model (1) with the half-bandwidth $\Delta_{1/2,I}$ = 2800 cm⁻¹ [15].

It is necessary to emphasize that following their chemical formula one can expect substantial second-order nonlinear optical effects, similar to those existed for the stilbenes [16].

In Fig. 4 are presented the experimental absorption spectra obtained in the THF solution with spectral resolution 1 nm. One can clearly see the existence of fourth principal spectral maxima. The obtained spectra are in a principal agreement with the theoretically calculated data obtained within a framework of TDDFT approach (see Fig. 5). For the convenience of readers all the data are presented in the table. One of the principal factors is the behavior of the chromophore in the polymer matrices, in particularly in the traditional PMMA matrices. Our earlier experience has shown [17] that the surrounding polymer matrices usually enhance polarizability of the investigated chromophore and favor an enhanced spectral shift of principal spectral maxima. To explore this influence in our case we have carried out the quantum-chemical simulations



Fig. 4. Experimental absorption spectra of the investigated molecule.



Fig. 5. Theoretically simulated absorption spectra obtained by the ADF program.

of the chromophore spectra embedded into the PMMA matrices. The results are presented in Figs. 4 and 5 and together with the data gathered in the table show that only for the chromophore **D** we obtain obvious red spectral shifts. The principal spectral maxima are shifted from 20 nm up to 50 nm to the longer wavelengths. At the same time this shift is vanishingly small for the **A**-**C** chromophores. This fact may have a principal importance during the use of investigated chromophore in the polymer matrices.

4. Conclusions

Complex experimental and theoretical investigations of UV-vis spectra for 1,4-diethoxy-2,5-bis[2-(5-methylthien-2-yl) ethenyl]benzene (A-C) and E,E isomer of 1,4-diisopropoxy-2,5-bis[2-(thien-2-yl)ethenyl]benzene (D) were done. We have established a good agreement between the calculated and experimentally measured optical spectra and spectral positions of principal spectral maxima. It is crucial that incorporation of the investigated chromophore into the PMMA matrices has an obvious red wavelength spectral shift only for the chromophore **D** (up to 40–50 nm). At the same time this spectral shift is vanishingly low for the chromophore molecule **A**–**C**. It may reflect a crucial influence of chromophore stereochemistry factor during incorporation of such chromophore in the polymer matrices.

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