Annelated tricyclic thiophenes and their photophysical properties
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Photochemical oxidative cyclization of 3-[(E)-2-(3,4-dimethoxyphenyl)vinyl]thiophene and its 15-crown-5-analogue (15-[(E)-2-(3-thienyl)vinyl]-2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaacyclopentadecine) affords the isomeric thiophene-containing fused aromatic compounds demonstrating photophysical properties different from those of initial styryl derivatives. E-Configuration of the initial styryl dye, 3-[(E)-2-(3,4-dimethoxyphenyl)vinyl]thiophene, has been proved by X-ray analysis.

The photocyclization of stilbenes (1,2-diarylethenes) provides a convenient approach to novel planar polyaromatic compounds, and their heterocyclic analogues are of significant interest as prospective materials for electroluminescent devices, organic conductors and photovoltaic systems.1–3 As a rule, the existing methods for the synthesis of polycyclic heteroatomic compounds are multi-stage and laborious.4,5 Photochemical transformations of 1,2-di(hetero)arylestilbenes are now actively used for the synthesis of various classes of organic compounds that are difficult to access by alternative synthetic strategies.6–10 Specifically, three different pathways of the initially formed tricyclic cyclohexadien-like structure are reported, namely, the reversed reaction, cyclization of 1-thienylstilbenes and oxidation of cyclohexadiene to form tricyclic annelated aromatic scaffold,11,12 and [1,1]-hydrogen shift followed by the destruction of the periophoric aromatic ring.13,14 The course of the reaction is governed by the preorganization of the double bond, heterocycle type, and reaction conditions, e.g., the acid concentration.15

Some examples of the photocyclization of 1,2-dithienyl- or 1-thienyl-2-arylestilbenes are known,18–21 however the diversity of the studied compounds is low for the assessment of the importance and the potential of this reaction. For instance, photocyclization of 1-thienyl-2-phenylnaphthalene with varied substituents on the phenyl side is not studied in detail yet.

In view of our experience in the synthesis of thiophene-containing stilbenes,22 now we report the oxidative intramolecular photocyclization of 3-styrylthiophenes containing 3,4-dimethoxy (1) and 15-crown-5 ether (2) groups attached or annelated to its phenyl side (Scheme 1)1 and photophysical characteristics of the obtained polycyclic products. The starting styryl derivatives were synthesized by the diethylphosphonate procedure ensuring the E-configuration of the double bond (see coupling constant for E-C=C-fragment in Figures S1, S5, Online Supplementary Materials, X-ray crystallography1 data for compound I in Figure 1, and the obtained polycyclic products. The starting styryl derivatives were synthesized by the diethylphosphonate procedure ensuring the E-configuration of the double bond (see coupling constant for E-C=C-fragment in Figures S1, S5, Online Supplementary Materials, X-ray crystallography1 data for compound I in Figure 1, and the
8.9, 11, 12, 14, 15, 17, 18-Octahydrothieno[2′,3′:5,6]napth[2,3-b] furyl[1,4- 7, 10, 13-pentaoxacyclopentadecine 4b: yield 14%, mp 138–140 °C. 1H NMR (400 MHz, CDCl3) δ: 3.82 (m, 8 H, CH2O), 4.00 (m, 4 H, CH2O), 4.27 (m, 2 H, CH2O), 4.32 (m, 2H, CH2O), 7.25 (s, 1H, H-6), 7.35 (s, 1 H, H-20), 7.41 (d, 1H, Th, 3J 5.3 Hz), 7.42 (d, 1H, Th, 3J 5.3 Hz), 7.58 (d, 1H, Ar, 3J 8.6 Hz), 7.70 (d, 1H, Ar, 3J 8.6 Hz). 13C NMR (APT) (100 MHz, CDCl3) δ: 60.39, 68.56, 69.26, 69.33, 70.24, 71.11, 70.33, 71.04 (CH2), 60.39, 68.56, 69.26, 69.33, 70.24, 71.11, 70.33, 71.04 (CH2), 104.83, 109.77, 120.26, 123.85, 124.05, 125.16 (Caryl), 124.41, 126.12, 136.21, 136.28, 148.63, 149.50 (Cquat). MS (ESI), m/z: 229 [M+Na]+.

Crystallographic data for 3099 observed reflections with Riso = 0.0772, wRiso = 0.214. Superscripts: (see Scheme 1) of the styrylthiophenes were calculated using the intensity data of the equivalent reflections. Intensities of 3758 independent reflections (Rint = 0.0270) out of 12685 collected were used in structure solution and refinement. The structure was solved by direct methods and refined by the full-matrix least-squares technique against F2 in anisotropic approximation. The positions of hydrogen atoms were calculated. Hydrogen atoms were refined in riding model with Uiso(H) equal to 1.5Uiso(C) and 1.2Uiso(C) of the connected methyl carbon and other carbon atoms. Due to low contribution of the minor disordered component of the thiophene ring to the diffraction, the bond lengths and thermal parameters of this component were constrained to be the same as for the major component (SHEXL SAME and EADP instructions). The refinement converged to R1 = 0.0410 [calculated for 3099 observed reflections with I > 2σ(I)], wR2 = 0.1118 and GOF = 1.048. All calculations were performed with SHEXL software package. CCDC 1811313 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk.

Table 1 Calculated values of ground state energies of E-I conformers (see Scheme 1) and their fractions at 20 °C.

| E-I conformer | E/kcal mol⁻¹ | Calculated fraction (%) | Product |
|---------------|-------------|-------------------------|---------|
| a             | −9.467      | 51                      | 3a      |
| b             | −9.263      | 21                      | 4a      |
| c             | −8.929      | 10                      | 3b      |
| d             | −9.197      | 18                      | 4b      |

Spin system analysis. When irradiated, styrylthiophenes undergo E-Z-isomerization at the first stage (see Scheme 1), which can be evidenced by 1H NMR at the early stages of the reaction (for instance, see Figure S1). The Z-forms are further cyclized and an unstable non-aromatic intermediate product is formed, 2-thiényl rather than 4-thiényl position being involved in the reaction. At the last step, this intermediate is oxidized as two hydrogen atoms are removed giving rise to an aromatic product. Each of the starting compounds, 1 and 2, yields two photoproducts, i.e., 3a, 3b and 4a, 4b, respectively (see Scheme 1, Figures S2–S14).

Yields of products 3, 4 (see Scheme 1) are reasonable enough; moreover, their formation occurs from readily available styryl derivatives upon mercury lamp irradiation at room temperature for 30 min. Alternative synthetic pathways to similar fused compounds are laborious and multi-stage. Of particular interest is the fact that sterically hindered isomers 3a and 4a are formed in a higher yield. To rationalize such a preference, ground state energies of different conformers of the E-Ia–d were calculated by MOPAC2016 program with PM7 Hamiltonian as well as their equilibrium amounts were calculated using the Boltzmann distribution model (Table 1).

Isomerization of E-isomers leads to the corresponding Z-isomers a–d (see Scheme 1, Table 1). Due to low reactivity of C-atom in the 4-position of the thiophene residue, the participation of Z-isomers b and d in the cyclization reaction can be disregarded. Thus, the cyclic products 3a and 4a can be formed from a and c conformers of Z-isomer. Because of the low activation barrier of the rotation around a single bond, conformers b and c can easily transform into a and d, respectively. The ratio between fraction of Z-isomers a and b leading to product 3a and fraction of Z-isomers c and d giving product 4a is 72:28 (see Scheme 1). This ratio is close to that observed in synthesis (2.7:1). Thus, the calculations are in agreement with the experiment.

Table 2 shows the measured photochemical and photophysical characteristics (for details of measurements, see Online Supplementary Materials) of the styrylthiophenes 1, 2 and products.
of their photocyclization 3a,b and 4a,b. The absorption and emission spectra are presented in Figures S15–S18. As an example, Figure 2 shows the fluorescence decay curve for 3a in cyclohexane, corresponding data for the rest compounds are presented in Figures S19–S24. As shown by measurements, the quantum yields of the direct and reverse E→Z-isomerization reactions of 1 and 2 are sufficiently high (Table 2, measurement of quantum yields is described in Online Supplementary Materials). The data given in Table 2 indicate the following changes in characteristics between styryl derivatives and cyclic ones: (i) shift of absorption bands of 3a,b and 4a,b to the short wavelength region as compared with those for 1, 2; (ii) significant increase of the Stokes shift (up to 100 nm) in case of 3a,b and 4a,b; (iii) decrease in the quantum yield of fluorescence going from 1 and 2 to 3a,b and 4a,b; (iv) increase in the lifetime of the excited states for 3a,b and 4a,b. Low quantum yields of fluorescence in combination with a large Stokes shift and longer lifetimes can indicate the possibility of intersystem crossing to triplet states in photoproducts.

In summary, we have proposed mild conditions for the photocchemical cyclization of styrylthiophenes containing 3,4-dimethoxy and 15-crown-5 ether groups and conditions for the separation of the formed mixture of the photoproducts. Structures of isomeric cyclization products have been established and their photoc hemical and photophysical properties have been estimated.

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Table 2 Photochemical and photophysical characteristics of styryl dyes 1, 2 and products of their photocyclization 3a,b and 4a,b.

| Compound | λabs/nm | λem/nm | Φf (%) | Stokes shift/cm⁻¹ | ΦE→Z; ΦZ→E | ΦE→Z-(cyclized products) (%) | t₁/ns (%) | t₂/ns (%) |
|----------|---------|---------|--------|-------------------|-------------|---------------------------|----------|----------|
| 1        | 318     | 356     | 7.1    | 3360              |             |                          |          |          |
| 3a       | 367     | 4.5     | 10200  | –                 | 39, 44, 2.8 | 0.41 (100)                | –        |          |
| 3b       | 367     | 3.2     | 10200  | –                 | –           | 0.71 (91)                 | 6.74 (9) |          |
| 2        | 316     | 8.1     | 3560   | –                 | 44, 49, 4.5 | 0.28 (50)                 | 1.10 (50) |          |
| 4a       | 365     | 2.8     | 10200  | –                 | –           | 0.40 (100)                | –        |          |
| 4b       | 362     | 3.8     | 9550   | –                 | –           | 1.15 (97)                 | 7.40 (3) |          |

Figure 2 TCSPC histograms of (1) instrumental response, (2) fluorescence decay of 3a in cyclohexane and (3) the best biexponential fit of fluorescence decay in log scale. Excitation with 340 nm NanoLED.

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