Synthesis of crown-containing and related hetarylphenylacetylenes and acetylenyl dyes

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New 15(18)-crown-5(6)-containing and model methoxy-substituted 1-hetaryl-2-phenylacetylenes of the 4-pyridine and 2-benzothiazole series were synthesized using the addition of bromine to the ethylene fragment of the corresponding styrylheterocycles followed by dehydrobromination under the action of potassium *tert*-butoxide. The quaternization of the pyridylphenylacetylenes afforded new acetylenyl dyes. The structures of five synthesized compounds were determined by X-ray diffraction analysis.

Key words: styrylheterocycles, hetarylphenylacetylenes, crown ethers, synthesis, structure, X-ray diffraction analysis.

Neutral hetarylphenylacetylenes, their adducts with Lewis acids, and quaternary salts (acetylenyl dyes) have a complex of useful properties. These compounds fluoresce rather efficiently,¹⁻³ exhibit promising nonlinear optical properties,^{1,4,5} are capable of efficient electroluminescing,⁶ can serve as colorimetric and luminescent sensors to metal cations^{7,8} and be used as ligands in luminescent rare-earth metal complexes,⁹ form liquid crystals,¹⁰ and possess biological activity.^{11–14} Structural fragments of hetarylphenylacetylenes were used for the production of molecular wires¹⁵ and a large series of nanosized macrocyclic compounds.¹⁶

The introduction of a macroheterocyclic fragment into a hetarylphenylacetylene molecule in such a way that at least one its heteroatom would be conjugated with the chromophore moiety is considerably interesting from the viewpoint of development of a new type of optical molecular sensors to metal cations. It can be assumed that, unlike related crown-containing hetarylphenylethylenes,¹⁷ these compounds would have more promising cation-dependent optical characteristics due to a rigid structure of the chromogen and the absence of the major part of channels of excited state relaxation typical of hetarylphenylethylenes (*trans—cis*-isomerization, electrocyclic reaction, [2+2] photocycloaddition). However, a few crown-containing hetarylphenylacetylenes are known to date, for example, pyridylphenylacetylene with the aza-15-crown-5 fragment,¹⁸ monocrown-containing bis(phenylterpyridyl-acetylene),¹⁹ and bis(15-crown)-containing bis(acetylene) based on 2,2'-dipyridyl.²⁰ This is associated, to some extent, with poor availability of the starting compounds for the synthesis.

Hetarylphenylacetylenes were earlier synthesized by the bromination of 1-hetaryl-2-phenylethylenes at the C=C double bond in CCl₄ followed by dehydrobromination with KOH in ethanol^{21,22} or by the condensation of diphenyl 1-halogen-1-hetarylmethanephosphonates with benzalde-hydes in the presence of a strong base (Wittig reaction in the Horner–Emmons).²³ The synthesis of hetarylphenyl-acetylenes using cross-coupling (Sonogashira reaction and its modifications) became especially popular in the recent time (see, *e.g.*, Refs 2 and 24–27).

The preparation of crown-containing hetarylphenylacetylenes using the Wittig or Sonogashira reactions requires fairly complicated and labor-consuming preliminary synthesis of the starting compounds (phosphonate salts, phenylacetylenes, halogen- or ethynyl-substituted heterocycles), and the influence of the macrocyclic fragment in the occurrence of each stage of the multistage synthesis is hardly predictable. We assumed that comparatively easily accessible hetarylphenylethylenes, whose synthesis has sufficiently been developed^{28–32} by us, can

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be the best starting compounds for the preparation of crown-containing hetarylphenylacetylenes. In the present work, we studied the consecutive bromination—dehydrobromination reactions of crown-containing and model methoxy-substituted hetarylphenylethylenes 1-3 of the 4-pyridine, 2-benzothiazole, and 4-quinoline series in order to optimize the synthesis conditions for the corresponding hetarylphenylacetylenes.

At first we attempted to synthesize acetylene compounds **4b** and **5** by analogy with the synthesis of di-(4-pyridyl)acetylene, which is readily formed³³ on heating of 1,2-di(4-pyridyl)ethylene with a bromine solution in concentrated HBr followed by dehydrobromination by Bu^tONa in *tert*-butyl alcohol. However, according to the ¹H NMR spectroscopy data, poorly separable mixtures of compounds **4** and **5** and their bromo-containing derivatives at position 6' of the benzene ring were obtained. Evidently, under these conditions, the bromination of the electron-excessive dimethoxy-substituted benzene fragment of compounds **1b** and **2** or in their bromination products at the C=C bond occurs simultaneously.

The side bromination at the benzene fragment was avoided when the first stage was carried out under milder conditions: in a CH_2Cl_2 or $CHCl_3$ solution at ambient temperature (Scheme 1). The 1,2-dibromoethanes formed were not purified and treated with a Bu^tOK solution in boiling *tert*-butyl alcohol to give target acetylenes **4a**–**d** and **5** in 35–59% yields. Under these conditions, 4-styrylquinoline **3** yielded a mixture of products, from

which quinolylphenylacetylene bromo-substituted derivative $\mathbf{6}$ was isolated by crystallization.

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The quaternization of pyridylphenylacetylenes **4a**,**c** afforded new acetylenyl dyes **7a**–**d** in 47–100% yields (Scheme 2). The long-wavelength absorption of dyes **7a**–**d** $(\lambda_{max} = 362-379 \text{ nm})$ is bathochromically shifted relative to the bands of the starting pyridylphenylacetylenes **4a** and **4c** ($\lambda_{max} = 310$ and 315 nm, respectively), which unambiguously due to the more favorable intramolecular charge transfer from the donor benzene fragment to the acceptor pyridine residue bearing a positive charge compared to the neutral pyridine residue.

Our preliminary studies by spectrophotometric titration of the complexation properties of 15-crown-5-containing acetylenyl dye **7d** showed that in a 0.01 *M* solution of Et₄NClO₄ in MeCN this ligand formed 1 : 1 complexes with Na⁺ and Ca²⁺ ions (logK = 3.35±0.05 and 4.14±0.05, respectively). For the formation of complexes **7d** · Na⁺ and **7d** · Ca²⁺, the hypsochromic shift of the long-wavelength absorption band maximum attains 16 and 32 nm, respectively. Under these conditions, model methoxy-containing dye **7a** forms no complexes with these metal cations.

Neutral pyridylphenylacetylenes **4b,d** and acetylenyl dyes **7a,b,d** were obtained as single crystals and studied by X-ray diffraction analysis. The structures of these compounds are shown in Figs 1 and 2; the same numeration of one-type atoms differed from the IUPAC rules was used for convenience of comparison of the geometric parameters. Selected bond lengths and angles are listed in Table 1.



1, 4: $R^1 = OMe$, $R^2 = H$ (**a**), $R^1 = R^2 = OMe$ (**b**), $R^1 + R^2 = OCH_2(CH_2OCH_2)_nCH_2O$, n = 3 (**c**), 4 (**d**)



Схема 2

The carbon—carbon triple bond is localized in all compounds: the average value of the $C(6) \equiv C(7)$ bond length is 1.191(4) Å, whereas the lengths of the adjacent formally ordinary C(3)—C(6) and C(7)—C(8) bonds are 1.432(4) and 1.435(4) Å on the average, which is characteristic



Fig. 1. Structures of compounds **4b** and **4d**. Thermal ellipsoids are drawn with 50% probability.

of other crystalline pyridylphenylacetylenes (see, e.g., Refs 19, 34, and 35). Nevertheless, the conjugation over the whole chromophore is possible in compounds 4 and 7, which is indicated by its, as a whole, planar structure: the dihedral angle between the planes of the pyridine and benzene cycles does not exceed 17.6°. In spite of the low accuracy in determination of structures 4d and 7d, the following general tendencies in bond length distribution in the benzene rings of the acetylene compounds can be mentioned. Compounds 4b, 4d, and 7d are characterized by the weakly pronounced alternation of the bond lengths in the half of the C(8)-C(13)-C(12)-C(11) benzene ring, *i.e.*, the C(8)–C(13) and C(11)–C(12) bonds are slightly elongated (average values 1.408(4) and 1.416(4) Å) and the C(12)–C(13) bond length (average value 1.382(4) Å) is close to the standard value (1.39 Å). In the second half of the benzene ring of these compounds, C(8)-C(9)-C(10)-C(11), the bond lengths are more aligned: the average values are 1.393(4), 1.395(4), and 1.382(4) Å, respectively. A similar bond length distribution in the benzene rings of the molecules has earlier been observed^{30,36,37} in crystals of the styryl and butadienyl dyes and bis(crown)containing stilbenes. The reproducibility of the effect of nonsymmetrical bond distribution in two halves of the benzene ring is reflected, most likely, by the inconsistent electronic influence of two AlkO substituents in the metaand *para*-positions with respect to the Pv-C=C group. This indicates π -conjugation over the whole chromophore



Fig. 2. Structures of dyes $7\mathbf{a} \cdot 0.5\mathbf{C}_6\mathbf{H}_6$ (two independent molecules), $7\mathbf{b} \cdot 0.5\mathbf{C}_6\mathbf{H}_6$, and $7\mathbf{d} \cdot 0.25\mathbf{C}_6\mathbf{H}_6 \cdot 1.75\mathbf{H}_2\mathbf{O}$. Thermal ellipsoids are drawn with 50% probability.

Parameter	4b	4d	7a*	7b	7d
Bond length			d∕Å		
C(3) - C(6)	1.4320(13)	1.458(7)	1.425(3), 1.427(3)	1.426(3)	1.426(6)
C(6) - C(7)	1.2010(14)	1.155(6)	1.194(3), 1.192(3)	1.203(3)	1.200(6)
C(7) - C(8)	1.4367(13)	1.446(6)	1.436(3), 1.428(3)	1.427(3)	1.433(6)
C(8) - C(9)	1.3903(14)	1.390(6)	1.393(3), 1.396(3)	1.399(3)	1.399(6)
C(8)-C(13)	1.4077(14)	1.411(6)	1.400(3), 1.396(3)	1.410(3)	1.404(5)
C(9)-C(10)	1.3953(13)	1.409(5)	1.385(3), 1.387(3)	1.379(3)	1.382(6)
C(10)-C(11)	1.3836(13)	1.381(6)	1.383(3), 1.390(3)	1.399(3)	1.381(5)
C(11) - C(12)	1.4141(13)	1.410(6)	1.396(3), 1.390(4)	1.399(3)	1.424(5)
C(12)-C(13)	1.3845(13)	1.390(6)	1.370(3), 1.385(4)	1.382(3)	1.372(5)
O(1)–C(11)	1.3635(11)	1.363(5)	1.368(3), 1.364(3)	1.368(2)	1.353(4)
O(1) - C(14)	1.4365(12)	1.454(5)	1.422(3), 1.435(4)	1.442(3)	1.443(4)
O(2)-C(12)	1.3612(11)	1.365(5)	_	_ `	1.364(4)
O(2)-C(15)	1.4328(12)	1.426(5)	—	—	1.436(4)
Bond angle			ω/deg		
C(11) - O(1) - C(14)	117.01(7)	116.0(4)	117.8(2),117.4(2)	117.67(18)	117.8(3)
C(12) - O(2) - C(15)	117.17(8)	119.2(4)	_	_`´	118.3(3)
O(1) - C(11) - C(10)	124.84(8)	125.5(4)	124.3(2),124.2(2)	124.6(2)	126.7(3)
O(1) - C(11) - C(12)	115.34(8)	115.1(4)	115.9(2),115.6(2)	115.02(18)	113.9(3)
O(2) - C(12) - C(11)	114.86(8)	115.0(4)	_		114.6(3)
O(2) - C(12) - C(13)	125.16(9)	124.5(4)	—	—	125.3(3)
Torsion angle			φ/deg		
C(14) = O(1) = C(11) = C(10)	7.1	9.6	4.0 1.3	3.6	11.0
C(15)-O(2)-C(12)-C(13)	-3.7	-10.1	_	_	-14.2
Dihedral angle			τ/deg		
N(1),C(1)C(5)/C(8)C(13) 17.6	12.2	10.1, 6.7	2.6	5.7

Table 1. Selected bond lengths (d) and bond (ω), torsion (φ), and dihedral (τ) angles in compounds **4b**,d and **7a**,b,d

* For two independent molecules.

involving the preferentially half of the C(8)-C(9)-C(10)-C(11) benzene ring. In dyes **7a**,**b** containing only one methoxy substituent in the benzene ring in the *para*position to the Py-C=C group, the electronic influence of the substituents is consistent and, as a consequence, the bond length distribution in the benzene ring corresponds to the contribution to the symmetrical quinoid structure: the C(8)-C(9), C(8)-C(13), C(10)-C(11), and C(11)-C(12) bonds are slightly elongated (the average value is 1.396(3) Å), whereas the C(9)-C(10) and C(12)-C(13) bonds are slightly shortened (average value 1.381(3) Å). This bond length distribution in the benzene ring also confirms the conjugation in the chromophore fragment of **7a**,**b**.

In spite of the steric repulsion between the *ortho*-arranged alkoxyl substituents in compounds **4b**,**d** and **7d**, the exocyclic (towards the benzene ring and macrocycle) bond angles at the C(11) and C(12) atoms are considerably enlarged (the O(1)–C(11)–C(10) and O(2)–C(12)–C(13) are 125.3(3)° on the average), whereas the conjugated are smaller (the O(1)–C(11)–C(12) and O(2)–C(12)–C(11)

angles are $114.8(3)^{\circ}$ on the average) (see Table 1). This deformation of the bond angles relative to the ideal value of 120° characteristic of the most part of 1,2-dialkoxybenzene should result in bringing together of the ortho-arranged oxygen atoms, *i.e.*, in the enhancement of their steric repulsion, and can be explained only in terms of electronic effects. Earlier^{37–39} we ascribed this phenomenon to the efficient conjugation of lone electron pairs (LEP) of the indicated O atoms lying on the p-orbitals with the benzene ring. Similar deformation of the exocyclic bind angles at the C(11) atom is observed in dyes 7a,b having only one methoxy group in the benzene ring, which also indicates the efficient conjugation of the LEP of the oxygen atom with the benzene ring. This conjugation is favored by the conformation of the C(14)-O(1)-C(11)-C(10) and C(15)-O(2)-C(12)-C(13) fragments, when the indicated torsion angles are fairly small (from -14.2° to 11.0°), *i.e.*, close to the value of 0° necessary for the maximum conjugation to occur. Conjugation is also indicated by the close to sp²-hybrid state of the O atoms attached to the benzene ring, which is characterized by the increased values of the C(11)–O(1)–C(14) and C(12)–O(2)–C(15) bond angles (on the average, 117.6(2)°) compared to the C_{Alk}–O–C_{Alk} angles (on the average, 113.6(3)° in compounds **4d** and **7d**), and by the shortened O(1)–C(11) and O(2)–C(12) bonds (average value 1.363(3) Å) compared to the O(1)–C(14) and O(2)–C(15) bonds (average value 1.436(3) Å).

In structure $7d \cdot 0.25C_6H_6 \cdot 1.75H_2O$, the $H_2O(1W)$ water molecule forms the weak forked hydrogen bond with the O(1) and O(2) oxygen atoms of the macrocycle. The hydrogen bond is characterized by the following parameters: the O(1W)-H...O(1) and O(1W)-H...O(2) bond lengths are 2.38(4) and 2.20(3) Å, the angles at the H atom are 138(5) and 155(6)°. The second hydrogen atom of this water molecule is not located.

Thus, the synthesis of new 1-(4-pyridyl)-2-phenylacetylenes and 1-(2-benzothiazolyl)-2-phenylacetylene bearing the crown fragment or methoxy groups in the benzene ring was developed, which includes the addition of bromine to the ethylene fragment of the corresponding styrylheterocycles followed by dehydrobromination under the action of a strong base. It was shown that the obtained pyridylphenylacetylenes can be used for the synthesis of new acetylenyl dyes. The crown-containing acetylenyl dyes can serve as efficient molecular sensors to alkaline and alkaline-earth metal cations.

Experimental

Melting points (uncorrected) were measured in capillaries on a Mel-Temp II instrument. Mass spectra were recorded on a Varian MAT 311A instrument at an ionization energy of 70 eV with direct sample injection into the ionization region. Elemental analyses were carried out at the Laboratory of Microanalysis of the A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences (Moscow, Russia). TLC monitoring was performed on the DC-Alufolien Kieselgel 60 F254 plates (Merck). Column chromatography was carried out on SiO₂ (Kieselgel 60, 0.063-0.100 mm, Merck or Kieselgel 60, 0.035-0.070 mm, Fluka). ¹H and ¹³C NMR spectra were recorded on a Bruker DRX-500 spectrometer (500.13 and 125.76 MHz, respectively) in DMSO-d₆ using the signal from the solvent as an internal standard (δ_H 2.50, δ_C 39.43). Chemical shifts were measured with the accuracy to 0.01 ppm, and spin-spin coupling (SSC) constants were determined with the accuracy to 0.1 Hz. The 2D homonuclear ¹H-¹H ROESY and heteronuclear ¹H–¹³C COSY (HSQC and HMBC) spectra were used for the assignment of signals from protons and carbons. The 2D experiments were carried out using standard parameters from the Bruker program package. The duration of mixing in the ROESY experiment was 300 µs, and the HMBC experiment was optimized for the constant $J_{\rm H,C}$ = 8 Hz. UV spectra were recorded on a Shimadzu UV-3101PC spectrophotometer in the range from 200 to 600 nm with an increment of 1 nm (MeCN or water, 1-cm quartz cell, room temperature).

Potassium *tert*-butoxide, methyl iodide, ethyl *p*-toluenesulfonate, 70% perchloric acid, and 1,3-propane sultone (Aldrich) were used without additional purification. Styrylheterocycles 1a-d, 2, and 3 were synthesized according to known procedures. $^{28-30,32,40}$

Synthesis of acetylenes 4a-d and 5 (general procedure). A solution of bromine (51 mg, 0.32 mmol) in CHCl₃ (1.5 mL) in the case of 1a,b and 2 or in CH₂Cl₂ (1.5 mL) in the case of 1c,d was added to a solution of styrylheterocycle 1a-d or 2 (0.3 mmol) in $CHCl_3$ (5–7 mL) in the case of **1a**,**b** and **2** or in CH₂Cl₂ (15–20 mL) in the case of 1c,d, and the mixture was kept for 3-4 days at ~20 °C in the dark until the initial styrylheterocycle disappeared (TLC monitoring). Chloroform or CH₂Cl₂ (30 mL) was added to the reaction mixture, the mixture was washed with a 2% aqueous solution of Na₂SO₃, and the organic solvent was thoroughly evaporated in vacuo. Potassium *tert*-butoxide (0.56 g, 5 mmol) in absolute Bu^tOH (10 mL) was added to the dry residue, and the mixture was heated with stirring for 3–4 h at 80 °C. Water (0.2 mL) was added to the reaction mixture, the solvent was evaporated *in vacuo*, water (50 mL) was added to the residue, and the organics was extracted with benzene $(2 \times 30 \text{ mL})$ in the case of synthesis of compounds 4a,b, **5** or CH₂Cl₂ (3×20 mL) for the synthesis of compounds **4c**,**d**. The organic extracts were evaporated in vacuo, and the residue was chromatographed on SiO2, using the following eluents: benzene-EtOAc (5:1) in the case of 4a, a gradient benzene-EtOAc mixture to 60% of the latter in the case of 4b, a gradient benzene-MeCN mixture to 50% of the latter in the case of 4c, benzene—EtOAc (1:1) and then benzene—PrⁱOH (4:1) in the case of 4d, and benzene-EtOAc (9:1) in the case of 5.

4-[(4-Methoxyphenyl)ethynyl]pyridine (4a) was obtained in 59% yield as a slightly yellowish substance with m.p. 96–98 °C (from hexane) (*cf.* Ref. 22: m.p. 104.5–105.5 °C). Found (%): C, 80.03; H, 5.10; N, 6.39. C₁₄H₁₁NO. Calculated (%): C, 80.36; H, 5.30; N, 6.69. ¹H NMR (23 °C), δ : 3.82 (s, 3 H, MeO); 7.03 (d, 2 H, H(3'), H(5'), J = 8.8 Hz); 7.50 (d, 2 H, H(3), H(5), J = 6.0 Hz); 7.57 (d, 2 H, H(2'), H(6'), J = 8.8 Hz); 8.61 (d, 2 H, H(2), H(6), J = 6.0 Hz). ¹³C NMR (30 °C), δ : 55.22 (MeO); 85.48 (C=<u>C</u>Py); 93.90 (<u>C</u>=CPy); 112.96 (C(1')); 114.42 (C(3'), C(5')); 125.03 (C(3), C(5)); 130.48 (C(4)); 133.30 (C(2'), C(6')); 149.75 (C(2), C(6)); 160.11 (C(4')). UV (MeCN, $C = 5 \cdot 10^{-5}$ mol L⁻¹), λ_{max}/nm (ϵ): 310 (23000), 298 (23100), 248 (10200). MS, m/z (I_{rel} (%)): 209 [M]⁺ (42), 194 (20), 166 (30), 140 (8), 139 (25), 71 (8), 59 (15), 58 (100), 57 (8), 55 (8).

4-[(3,4-Dimethoxyphenyl)ethynyl]pyridine (4b) was synthesized in 57% yield as a slightly yellowish substance with m.p. 113–114 °C (from hexane). Found (%): C, 75.36; H, 5.37; N, 5.71. C₁₅H₁₃NO₂. Calculated (%): C, 75.30; H, 5.48; N, 5.85. ¹H NMR (27 °C), & 3.80 (s, 6 H, 2 MeO); 7.00 (d, 1 H, H(5'), J = 8.3 Hz); 7.16 (d, 1 H, H(2'), J = 1.7 Hz); 7.19 (dd, 1 H, H(6'), J = 8.3 Hz, J = 1.7 Hz); 7.47 (d, 2 H, H(3), H(5), J = 6.0 Hz); 8.60 (d, 2 H, H(2), H(6), J = 6.0 Hz). ¹³C NMR (27 °C), &: 55.43 (MeO); 55.50 (MeO); 85.25 (C=<u>C</u>Py); 94.32 (<u>C</u>=CPy); 111.71 (C(5')); 112.98 (C(1')); 114.45 (C(2')); 125.05 (C(3), C(5)); 125.20 (C(6')); 130.53 (C(4)); 148.57 (C(3')); 149.77 (C(2), C(6)); 150.20 (C(4')). UV (MeCN, $C = 5 \cdot 10^{-5}$ mol L⁻¹), λ_{max}/nm (&: 316 (19 400), 292 (15 400), 241 (15 400). MS, m/z (I_{rel} (%)): 239 [M]⁺ (100), 224 (18), 196 (30), 168 (10), 167 (14), 166 (6), 153 (17), 127 (17), 126 (8), 58 (18).

4-(2,3,5,6,8,9,11,12-Octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylethynyl)pyridine (4c) was synthesized in 39% yield as a slightly yellowish substance with m.p. 126-128 °C (from hexane). Found (%): C, 68.17; H, 6.14; N, 3.71. C₂₁H₂₃NO₅. Calculated (%): C, 68.28; H, 6.28; N, 3.79. ¹H NMR (25 °C), δ: 3.62 (m, 8 H, 4 CH₂O); 3.77 (m, 4 H, 2 C<u>H</u>₂CH₂OAr); 4.09 (m, 4 H, 2 C<u>H</u>₂OAr); 7.01 (d, 1 H, H(5'), J = 8.2 Hz); 7.16 (d, 1 H, H(2'), J = 1.9 Hz); 7.18 (dd, 1 H, H(6'), J = 8.2 Hz, J = 1.9 Hz); 7.48 (d, 2 H, H(3), H(5), J = 5.8 Hz); 8.61 (d, 2 H, H(2), H(6), J = 5.8 Hz). ¹³C NMR (23 °C), δ: 68.23 (CH₂OAr); 68.44 (CH₂CH₂OAr); 68.55 (CH₂OAr); 68.62 (CH₂CH₂OAr); 69.56 (CH₂O); 69.61 (CH₂O); 70.45 (2 CH₂O); 85.26 (C=CPy); 94.26 (C=CPy); 113.07 (C(1')); 113.25 (C(5')); 116.22 (C(2')); 125.06 (C(3), C(5)); 125.43 (C(6')); 130.48 (C(4)); 148.23 (C(3')); 149.80 (C(2), C(6)); 149.98 (C(4')). UV (MeCN, C = = $5 \cdot 10^{-5}$ mol L⁻¹), λ_{max}/mm (ε): 315 (23 000), 293 (18 500), 242 (17 000). MS, m/z (I_{rel} (%)): 369 [M]⁺ (14), 238 (12), 237 (100), 111 (13), 101 (16), 98 (31), 77 (19), 57 (32), 56 (25), 53 (21).

4-(2,3,5,6,8,9,11,12,14,15-Decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecin-18-ylethynyl)pyridine (4d) was synthesized in 35% yield as a slightly yellowish substance with m.p. 118–120 °C (from hexane). Found (%): C, 66.60; H, 6.54; N, 3.20. $C_{23}H_{27}NO_6$. Calculated (%): C, 66.81; H, 6.58; N, 3.39. ¹H NMR (23 °C), δ: 3.53 (s, 4 H, 2 CH₂O); 3.56 (m, 4 H, 2 CH₂O); 3.62 (m, 4 H, 2 CH₂O); 3.76 (m, 4 H, 2 CH₂CH₂OAr); 4.14 $(m, 4 H, 2 CH_2OAr);$ 7.03 (d, 1 H, H(5'), J = 8.1 Hz); 7.17 (br.s, 1 H, H(2')); 7.18 (dd, 1 H, H(6'), J = 8.1 Hz, J = 1.8 Hz); 7.50 (d, 2 H, H(3), H(5), J = 6.0 Hz); 8.61 (d, 2 H, H(2), H(6), J = 6.0 Hz). ¹³C NMR (30 °C), δ : 68.09 (<u>C</u>H₂OAr); 68.15 (<u>CH</u>₂OAr); 68.44 (<u>CH</u>₂CH₂OAr); 68.49 (<u>C</u>H₂CH₂OAr); 69.63 (2 CH₂O); 69.71 (2 CH₂O); 69.81 (2 CH₂O); 85.22 (C=<u>C</u>Py); 94.29 (C=CPy); 112.83 (C(5')); 112.96 (C(1')); 115.63 (C(2')); 125.02 (C(3), C(5)); 125.24 (C(6')); 130.48 (C(4)); 147.90 (C(3')); 149.62 (C(4')); 149.76 (C(2), C(6)). UV (MeCN, $C = 5 \cdot 10^{-5} \text{ mol } \text{L}^{-1}$), $\lambda_{\text{max}}/\text{nm}$ (ϵ): 320 (21 500), 293 (16 300), 243 (16 400). MS, m/z (I_{rel} (%)): 413 [M]⁺ (42), 325 (45), 237 (100), 222 (88), 210 (85), 181 (76), 152 (60), 111 (61), 73 (57), 71 (50).

2-[(3,4-Dimethoxyphenyl)ethynyl]-1,3-benzothiazole (5) was synthesized in 53% yield as a slightly yellowish substance with m.p. 91-93 °C (from hexane). Found (%): C, 69.16; H, 4.32; N, 4.62. C₁₇H₁₃NO₂S. Calculated (%): C, 69.13; H, 4.44; N, 4.74. ¹H NMR (30 °C), δ: 3.83 (s, 6 H, 2 MeO); 7.06 (d, 1 H, H(5'), J = 8.3 Hz; 7.27 (d, 1 H, H(2'), J = 1.6 Hz); 7.31 (dd, 1 H, H(6'), J = 8.3 Hz, J = 1.6 Hz; 7.53 (m, 1 H, H(6)); 7.59 (m, 1 H, H(5)); 8.05 (d, 1 H, H(4), J = 8.1 Hz); 8.13 (d, 1 H, H(4))H(7), J = 7.7 Hz). ¹³C NMR (30 °C), δ : 55.53 (MeO); 55.60 (MeO); 81.35 (C=CHet); 96.47 (C=CHet); 111.46 (C(1')); 111.86 (C(5')); 114.59 (C(2')); 122.05 (C(7)); 122.91 (C(4)); 125.79 (C(6')); 126.27 (C(6)); 126.88 (C(5)); 134.60 (C(7a)); 147.84 (C(2)); 148.65 (C(3')); 150.93 (C(4')); 152.48 (C(3a)). UV (MeCN, $C = 5 \cdot 10^{-5} \text{ mol } L^{-1}$), $\lambda_{\text{max}}/\text{nm}$ (ϵ): 348 (24 000), 336 (25 900). MS, m/z (I_{rel} (%)): 295 [M]⁺ (100), 280 (75), 252 (69), 237 (41), 224 (49), 223 (58), 209 (34), 183 (40), 147 (34), 69 (48).

4-[(2-Bromo-4,5-dimethoxyphenyl)ethynyl]quinoline (6). A solution of bromine (83 mg, 0.52 mmol) in CHCl₃ (1.1 mL) was added to a solution of styrylquinoline **3** (50 mg, 0.17 mmol) in CHCl₃ (5 mL), and the mixture was kept for 4 days at ~20 °C in the dark. Chloroform (10 mL) was added to the mixture, which was washed with a 2% aqueous solution of Na_2SO_3 (5 mL), and the organic solvent was thoroughly evaporated *in vacuo*. A solution of Bu^tOK (0.76 g, 6.8 mmol) in absolute Bu^tOH (10 mL) was added to the dry residue (103 mg), and the mixture was heated for 3 h with stirring at 80 °C. Water (0.5 mL) was added to the reaction mixture, the solvent was evaporated *in vacuo*, and the residue was chromatographed on SiO₂, using as an eluent a gradient benzene-EtOAc mixture to 50% of the latter. One fraction (43 mg) containing a mixture of the compounds was collected (¹H NMR monitoring) and crystallized by the slow evaporation of the solution in a hexane-CHCl₃ mixture at ~20 °C. Compound 6 was obtained in a yield of 19 mg (30%) as yellowish spherulites with m.p. 105–107 °C. Found (%): C, 61.74; H, 3.85; N, 3.74. C₁₉H₁₄BrNO₂. Calculated (%): C, 61.97; H, 3.83; N, 3.80. ¹H NMR (27 °C), δ: 3.85 (s, 3 H, 5'-MeO); 3.87 (s, 3 H, 4'-MeO); 7.36 (s, 1 H, H(3')); 7.41 (s, 1 H, H(6')); 7.74 (d, 1 H, H(3), J = 4.5 Hz); 7.78 (m, 1 H, H(6); 7.87 (m, 1 H, H(7)); 8.10 (d, 1 H, H(8), J = 8.5 Hz); 8.51 (d, 1 H, H(5), J = 8.8 Hz); 8.95 (d, 1 H, H(2), J = 4.5 Hz). ¹³C NMR (25 °C), δ: 55.92 (5'-MeO); 56.09 (4'-MeO); 87.42 (C=CHet); 97.38 (C=CHet); 114.68 (C(1')); 115.47 (C(3'));115.84 (C(6')); 116.76 (C(2')); 123.51 (C(3)); 125.72 (C(5)); 126.58 (C(4a)); 127.71 (C(6)); 128.23 (C(4)); 129.51 (C(8)); 130.21 (C(7)); 147.51 (C(8a)); 148.17 (C(5')); 150.10 (C(2)); 150.90 (C(4')). UV (MeCN, $C = 5 \cdot 10^{-5} \text{ mol } L^{-1}$), $\lambda_{\text{max}}/\text{nm}$ (ϵ): 352 (21 500), 340 (21 300), 256 (17 700), 239 (29 400). MS, m/z $(I_{\rm rel} (\%))$: 369 [M]⁺ with ⁸¹Br (100), 367 [M]⁺ with ⁷⁹Br (98), 245 (35), 230 (11), 202 (16), 185 (10), 175 (30), 101 (14), 83 (9), 59 (15).

1-Methyl-4-[(4-methoxyphenyl)ethynyl]pyridinium iodide (7a). Methyl iodide (47 μ L, 0.75 mmol) was added to a solution of compound 4a (31 mg, 0.15 mmol) in CH₂Cl₂ (1 mL), and the mixture was kept for 6 days at ~20 °C. The solvent was evaporated in vacuo, and the residue was triturated in benzene (3 mL), filtered off, washed with benzene (2×3 mL), and dried in air. Dye 7a was obtained in a yield of 52 mg (100%) as a yellowishgreen powder with m.p. 188–190 °C (from MeCN-benzene). Found (%): C, 51.48; H, 4.01; N, 3.97. C₁₅H₁₄INO. Calculated (%): C, 51.30; H, 4.02; N, 3.99. ¹H NMR (28 °C), δ: 3.84 (s, 3 H, MeO); 4.30 (s, 3 H, MeN); 7.10 (d, 2 H, H(3'), H(5'), J = 8.8 Hz; 7.67 (d, 2 H, H(2'), H(6'), J = 8.8 Hz; 8.18 (d, 2 H, H(3), H(5), J = 6.6 Hz; 8.94 (d, 2 H, H(2), H(6), J = 6.6 Hz). ¹³C NMR (28 °C), δ: 47.54 (MeN); 55.47 (MeO); 84.92 (C=<u>C</u>Py); 103.17 (C=CPy); 111.46 (C(1')); 114.78 (C(3'), C(5')); 128.34 (C(3), C(5)); 134.36 (C(2'), C(6')); 138.61 (C(4)); 145.22 (C(2), C(6)); 161.32 (C(4')). UV (MeCN, $C = 5 \cdot 10^{-5} \text{ mol } L^{-1}$), $\lambda_{\text{max}}/\text{nm}$ (ϵ): 363 (28 200), 247 (27 500).

1-Ethyl-4-[(4-methoxyphenyl)ethynyl]pyridinium perchlorate (7b). A mixture of compound 4a (40 mg, 0.19 mmol) and ethyl *p*-toluenesulfonate (115 mg, 0.57 mmol) was heated for 4 h at 90 °C (oil bath). The resulting mixture was triturated with benzene ($2 \times 5 \text{ mL}$) at ~20 °C and then heated at 80 °C with 10 mL of benzene. The undissolved vellow substance was separated by decantation and dissolved in MeOH (2 mL). Then 70% perchloric acid (33 µL, 0.38 mmol) was added, and the mixture was cooled to -10 °C. The precipitate formed was rapidly filtered off, washed with benzene (2×5 mL), and dried in air. Dye 7b was obtained in a yield of 31 mg (47%) as a yellow powder with m.p. 136-138 °C (from MeOH). Found (%): C, 58.30; H, 4.60; N, 4.15. C₁₆H₁₆ClNO₅•0.15C₆H₆. Calculated (%): C, 58.08; H, 4.87; N, 4.01. ¹H NMR (30 °C), δ: 1.54 (t, 3 H, <u>Me</u>CH₂, J = 7.3 Hz; 3.85 (s, 3 H, MeO); 4.58 (q, 2 H, MeC<u>H</u>₂, J = 7.3 Hz); 7.10 (d, 2 H, H(3'), H(5'), J = 8.6 Hz); 7.68 (d, 2 H, H(2'), H(6'), J = 8.6 Hz; 8.20 (d, 2 H, H(3), H(5), J = 6.7 Hz; 9.05 (d, 2 H, H(2), H(6), J = 6.7 Hz).

Betaine 3-{4-[(4-methoxyphenyl)ethynyl]pyridinio-1-yl}propane-1-sulfonate (7c). 1,3-Propane sultone (37 μL, 0.42 mmol) was added to a solution of compound **4a** (59 mg, 0.28 mmol) in MeCN (2 mL), and the mixture was kept for 5 days at ~20 °C. The precipitate formed was filtered off, washed with MeCN (2 mL) and benzene (2×2 mL), and dried in air. Dye 7c was obtained in a yield of 50 mg (53%) as a cream-yellow powder with m.p. >265 °C (with decomp.) (MeCN-water-benzene). Found (%): C, 60.35; H, 5.03; N, 4.09. C₁₇H₁₇NO₄S•0.4H₂O. Calculated (%): C, 60.30; H, 5.30; N, 4.14. ¹H NMR (25 °C), δ: 2.23 (quintet, 2 H, CH₂CH₂SO₃, J = 7.0 Hz); 2.45 (t, 2 H, CH₂SO₃, J = 7.0 Hz); 3.84 (s, 3 H, MeO); 4.69 (t, 2 H, CH₂N, J = 6.9 Hz; 7.10 (d, 2 H, H(3'), H(5'), J = 8.7 Hz; 7.68 (d, 2 H, H(2'), H(6'), J = 8.7 Hz; 8.19 (d, 2 H, H(3), H(5), J = 6.6 Hz); 9.04 (d, 2 H, H(2), H(6), J = 6.6 Hz). ¹³C NMR (25 °C), δ : 27.15 (<u>CH</u>₂CH₂SO₃); 46.87 (CH₂SO₃); 55.50 (MeO); 59.20 (CH₂N); 85.14 (C=<u>C</u>Py); 103.35 (<u>C</u>=CPy); 111.57 (C(1')); 114.84 (C(3'), C(5')); 128.79 (C(3), C(5)); 134.45 (C(2'), C(6')); 139.04 (C(4)); 144.70 (C(2), C(6)); 161.41 (C(4')). UV (water, C == $5 \cdot 10^{-5} \text{ mol } L^{-1}$), λ_{max}/nm (ϵ): 362 (29 600), 247 (15 500).

1-Methyl-4-(2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecin-15-ylethynyl)pyridinium iodide (7d). Methyl iodide (40 μ L, 0.64 mmol) was added to a solution of compound 4c (11.0 mg, 29.8 μ mol) in anhydrous THF (1 mL), and the mixture was kept for 4 days at ~20 °C. The precipitate formed was filtered off, washed with benzene (2×1 mL), and dried in air. Dye 7d was obtained in a yield of 12.8 mg (84%) as a yellow powder with m.p. >230 °C (with decomp.). Found (%): C, 51.51; H, 5.07; N, 2.75. C₂₂H₂₆INO₅. Calculated (%): C, 51.67; H, 5.13; N, 2.74. ¹H NMR (26 °C), δ: 3.62 (m, 8 H, 4 CH₂O); 3.79 (m, 4 H, 2 CH₂CH₂OAr); 4.10 (m, 2 H, 3-CH₂OAr); 4.13 (m, 2 H, 4-CH₂OAr); 4.29 (s, 3 H, MeN); 7.08 (d, 1 H, H(5'), J = 8.3 Hz); 7.25 (d, 1 H, H(2'), J = 1.8 Hz); 7.31 (dd, 1 H, H(6'), J = 8.3 Hz, J = 1.8 Hz); 8.16 (d, 2 H, H(3), H(5), J = 6.7 Hz); 8.94 (d, 2 H, H(2), H(6), J = 6.7 Hz). ¹³C NMR (27 °C), δ: 47.53 (MeN); 68.24 (4-CH₂OAr); 68.41 (CH₂CH₂OAr); 68.53 (3-CH₂OAr, CH₂CH₂OAr); 69.46 (CH₂O); 69.54 (CH₂O); 70.41 (CH₂O); 70.43 (CH₂O); 84.71 (C=CPy); 103.60 (C=CPy); 111.49 (C(1')); 113.22 (C(5')); 116.63 (C(2')); 126.79 (C(6')); 128.32 (C(3), C(5)); 138.64 (C(4)); 145.27 (C(2), C(6)); 148.25 (C(3')); 151.30 (C(4')). UV (MeCN, C = 5 · 10⁻⁵ mol L⁻¹), λ_{max} /nm (ε): 379 (26 700), 248 (26 800).

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X-ray diffraction experiments. Crystals of pyridylphenylacetylenes **4b,d** were obtained by the slow evaporation of their solutions in a CH_2Cl_2 —hexane mixture at ~20 °C, and crystals of dyes **7a,b,d** were grown by the slow saturation of their solutions in MeCN with benzene vapors at ~20 °C.

Single crystals were placed on a Bruker SMART-CCD diffractometer under a cooled nitrogen flow (T = 120.0(2) K), where the crystallographic parameters and experimental reflection intensities on Mo-K α radiation were measured ($\lambda = 0.71073$ Å, graphite monochromator, ω scan mode). Experimental data were

Table 2. Parameters for crystals 4b , d and X-ray diffraction e	experiments
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Parameter	4b		
Molecular formula	C ₁₅ H ₁₃ NO ₂	C ₂₃ H ₂₇ NO ₆	
Molecular weight/g mol ⁻¹	239.26	309.35	
Crystal system	Monoclinic	Orthorhombic	
Space group	$P2_1/c$	$P2_{1}2_{1}2_{1}$	
a/Å	8.7887(2)	4.4952(5)	
b/Å	7.7121(2)	16.1797(17)	
c/Å	18.8813(4)	28.966(3)	
α/deg	90	90	
β/deg	95.0130(10)	90	
γ/deg	90	90	
$V/Å^3$	1274.87(5)	2106.7(4)	
Ζ	4	4	
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.247	1.304	
F(000)	504	880	
μ (Mo-K α)/mm ⁻¹	0.083	0.094	
Crystal size/mm	$0.26 \times 0.22 \times 0.18$	$0.36 \times 0.06 \times 0.04$	
Scan mode	ω	ω	
θ/deg	2.17-29.00	1.41-26.00	
Ranges of reflection indices	$-11 \le h \le 11, -10 \le k \le 9,$	$-2 \le h \le 5, -19 \le k \le 16,$	
	$-25 \le l \le 25$	$-35 \le l \le 35$	
Number of measured reflections	9623	10271	
Number of independent reflections	3375	4069	
	$[R_{\rm int} = 0.0170]$	$[R_{\rm int} = 0.2279]$	
Number of reflections with $I \ge 2\sigma(I)$	2847	1686	
Number of refinement variables	215	271	
<i>R</i> Factors for $I > 2\sigma(I)$	$R_1 = 0.0400, wR_2 = 0.1111$	$R_1 = 0.0750, wR_2 = 0.0804$	
Factors for all reflections	$R_1 = 0.0485, wR_2 = 0.1168$	$R_1 = 0.2387, wR_2 = 0.1005$	
Goodness-of-fit for F^2	1.069	0.871	
Residual electron density	-0.193/0.626	-0.223/0.315	
$/e \cdot Å^3$, ρ_{min}/ρ_{max}			

Parameter	7 a • 0.5C ₆ H ₆	7 b • 0.5C ₆ H ₆	$7d \cdot 0.25C_6H_6 \cdot 1.75H_2O$	
Molecular formula	C ₁₈ H ₁₇ INO	C ₁₉ H ₁₉ ClNO ₅	C _{23 5} H ₃₁ INO _{6 75}	
Molecular weight/g mol ^{-1}	390.23	376.80	562.39	
Crystal system	Monoclinic	Triclinic	Monoclinic	
Space group	$P2_1/c$	$P\overline{1}$	$P2_1/c$	
a/Å	10.0687(2)	6.6448(3)	20.0437(7)	
b/Å	32.5910(7)	8.8221(5)	6.8511(3)	
c/Å	10.5017(2)	16.5298(9)	19.4292(7)	
α/deg	90	100.596(2)	90	
β/deg	100.0660(10)	92.142(2)	106.611(2)	
γ/deg	90	107.251(2)	90	
$V/Å^3$	3393.08(12)	905.25(8)	2556.70(17)	
Z	8	2	4	
$d_{\rm calc}/{\rm g}~{\rm cm}^{-3}$	1.528	1.382	1.461	
F(000)	1544	394	1144	
$\mu(MoK\alpha)/mm^{-1}$	1.886	0.241	1.292	
Crystal size/mm	$0.30 \times 0.18 \times 0.07$	0.15×0.12×0.10	$0.48 \times 0.22 \times 0.01$	
Scan mode	ω	ω	ω	
θ/deg	2.05-29.00	2.47-28.00	2.12-29.00	
Ranges of reflection indices	$-13 \le h \le 13, -44 \le k \le 44,$	$-5 \le h \le 8, -11 \le k \le 8,$	$-27 \le h \le 26, -9 \le k \le 9,$	
	$-14 \le l \le 14$	$-21 \le l \le 21$	$-25 \le l \le 26$	
Number of measured reflections	29041	4885	19179	
Number of independent reflections	9017	3731	6781	
-	$[R_{int} = 0.0326]$	$[R_{int} = 0.0256]$	$[R_{int} = 0.0656]$	
Number of reflections with $I > 2\sigma(I)$	7364	2610	4714	
Number of refinement variables	515	311	303	
<i>R</i> Factors for $I > 2\sigma(I)$	$R_1 = 0.0272, wR_2 = 0.0573$	$R_1 = 0.0484, wR_2 = 0.1008$	$R_1 = 0.0451, wR_2 = 0.1068$	
<i>R</i> Factors for all reflections	$\vec{R_1} = 0.0389, w \vec{R_2} = 0.0599$	$R_1 = 0.0804, wR_2 = 0.1092$	$R_1 = 0.0765, wR_2 = 0.1165$	
Goodness-of-fit for F^2	1.009	1.016	0.956	
Residual electron density $/e \cdot Å^3$, ρ_{min}/ρ_{max}	-0.402/1.057	-0.327/0.247	-1.195/1.249	

Table 3. Parameters for crystals $7a \cdot 0.5C_6H_6$, $7b \cdot 0.5C_6H_6$ and $7d \cdot 0.25C_6H_6 \cdot 1.75H_2O$ and for X-ray diffraction experiments

processed according to the SAINT program.⁴¹ An X-ray absorption (by crystals of iodides 7a,b) correction was applied using the SADABS method. All structures were solved by direct methods and refined by least squares in the full-matrix anisotropic approximation for F^2 for non-hydrogen atoms (except for the atoms of the disordered solvate molecules in structure $7d \cdot 0.25C_6H_6 \cdot 1.75H_2O$, which were isotropically refined). Solvate benzene molecules were found in the independent part of the crystal cells of dyes 7a,b (in structure 7b the solvate benzene molecule lies in the symmetry center of the crystal). Five solvate water molecules and one benzene molecule were found in the independent part of the crystal cell of dye 7d, and this benzene molecule and water molecules O(2W), O(3W), O(4W), and O(5W) alternatively occupy the same site in the cell with site occupancies of 0.25: 0.30: 0.15: 0.15: 0.15, respectively. The position of hydrogen atoms at carbon atoms were calculated geometrically and refined in the isotropic approximation for structures **4b**, $7\mathbf{a} \cdot 0.5\mathbf{C}_6\mathbf{H}_6$ and $7\mathbf{b} \cdot 0.5\mathbf{C}_6\mathbf{H}_6$ or by the riding model for structures 4d and $7d \cdot 0.25C_6H_6 \cdot 1.75H_2O$. The hydrogen atoms of the water molecules in structure $7d \cdot 0.25C_6H_6 \cdot 1.75H_2O$ were not localized, except for one H atom of the H2O(1W) molecule. This hydrogen atom was refined in the isotropic approximation with restraint on the O(1W)—H bond length.

All calculations were performed using the SHELXTL-Plus program package.⁴² The crystallographic parameters and

characteristics of X-ray diffraction experiments are given in Tables 2 and 3. The coordinates of atoms and other experimental data were deposited with the Cambridge Crystallographic Data Centre (CCDC)* with the numbers 776884 (4b), 776885 (4d), 776886 ($7a \cdot 0.5C_6H_6$), 776887 ($7b \cdot 0.5C_6H_6$), and 776888 ($7d \cdot 0.25C_6H_6 \cdot 1.75H_2O$).

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