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Vacek, J.
2016

Dostupný z <http://www.nusl.cz/ntk/nusl-369614>

Dílo je chráněno podle autorského zákona č. 121/2000 Sb.

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Datum stažení: 20.04.2024

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A Short Overview of the Electrochemistry of Helical Polyaromatics

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Abstract

Here we describe the electrochemical behavior of a group of polyaromatics designated helicenes. These compounds are finding many applications in optoelectronics, catalysis and chiral separation. Thus it is important to investigate the electrochemical and optical behavior of helicenes with respect to improving their application potential and our knowledge of strategies for their surface immobilization. Electrochemical analyses were performed in acetonitrile and in aqueous media with glassy carbon and indium tin oxide electrodes. Specifically, [*n*]helicenes and their salts 1-butyl-3-(2-methyl[6]helicenyl)-imidazolium bromide and 3-([7]helicen-9-yl)thiophene were investigated. The application of acquired electrochemical data is discussed, especially in terms of optoelectronics and the construction of semi-conductive devices.

Key words: Helicene, Anodic reaction, Electropolymerization, ITO, Surface immobilization

Introduction

Helical polyaromatics such as helicenes exhibit a non-planar topology with a C₂-symmetric axis perpendicular to the axis of helicity as a result of the steric repulsive interaction between terminal aromatic rings. This makes them chiral, even though they have no center of chirality. The combination of chirality and an extended π -conjugated system makes helicenes and their derivatives promising candidates for circularly polarized luminescence devices, novel sensing technologies and chiral separation applications. Moreover, linking helicenes with intrinsically (semi)conductive polymers and other functional groups modulating their conductivity or solubility can produce currently unexplored new materials, polymers or composites. The current state of knowledge in this field is reviewed in ¹⁻⁴. In addition, a highly important aspect of the applicability of not only helicenes but also of other functional molecules in electronics is the development and optimization of immobilization or polymerization strategies enabling their accommodation into real devices and instrumentation.

To the best of our knowledge, there is no reported data on the redox/adsorption behavior and electropolymerization of helicenes. In this short contribution, we focused on the electrochemical investigation of racemic [5]helicene (**1**), [6]helicene (**2**), [7]helicene (**3**), 3-([7]helicen-9-yl)thiophene (**4**), and 1-butyl-3-(2-methyl[6]helicenyl)-imidazolium (**5**) as a bromide salt (Fig. 1). Applications of the acquired electrochemical data are discussed, specifically in terms of semi-conductive device construction and generally in terms of organic electronics and novel sensing strategies.

Experimental

Acetonitrile, p.a. (Sigma-Aldrich) + tetrabutylammonium perchlorate – TBAP (Fluka) or Britton-Robinson buffer (Sigma-Aldrich) were used as the supporting electrolytes in electrochemical experiments. Helicenes **1-3** were prepared according to a previously reported

protocol with slight modifications ⁵. 3-([7]helicen-9-yl)-thiophene **4** was synthesized from 3-thienylboronic acid and 9-bromo[7]helicene as described in our previously published communication ⁶. The salt **5** was prepared by starting from racemic 2-methyl[6]helicene, which undergoes radical bromination to yield 2-(bromomethyl)[6]helicene. Subsequent treatment with 1-butylimidazole leads to the corresponding salt 1-butyl-3-(2-methyl[6]helicenyl)-imidazolium bromide ⁷. Reverse-osmosis deionized water (Ultrapur, Watrex, CZ) was used throughout the study. The sample preparation and analyses were performed under ambient (air) conditions unless stated otherwise. Where appropriate, the solutions were deoxygenated with argon. The pH was measured with a pH/ORP Meter (HI2211) equipped with an HT 1131 electrode (HANNA Instruments, USA).

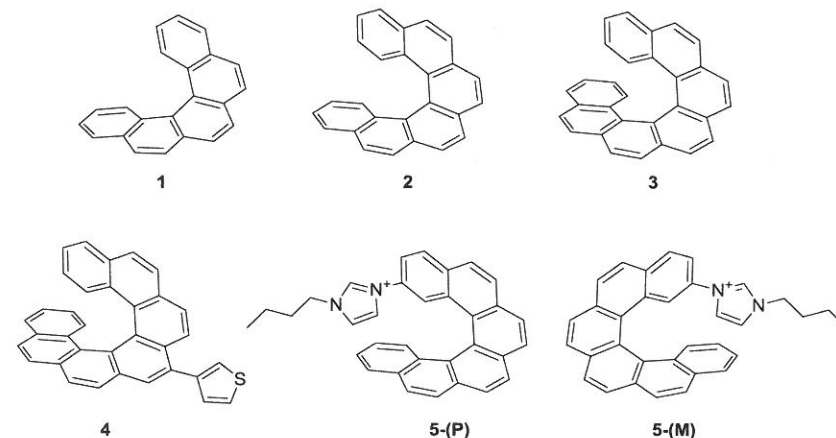


Fig. 1. Compounds involved in this study, [5]helicene (**1**), [6]helicene (**2**), [7]helicene (**3**), 3-([7]helicen-9-yl)thiophene (**4**), and 1-butyl-3-(2-methyl[6]helicenyl)-imidazolium (**5**) as both P and M enantiomers.

Voltammetric analyses and electropolymerization procedures were conducted using Nanoampere electrochemical workstation (L-Chem, Czech Republic). A CHI MF-2012 glassy carbon electrode (disc, 3 mm in diameter), Alfa Aesar type 38021 glassy carbon plates (4 cm × 1.6 cm × 1 mm), carbon fiber electrode (for details see refs. ^{8,9} and citations therein) and indium tin oxide (ITO) coated glass sq slide with surface resistivity of 8-12 Ω /sq, (Sigma Aldrich) were used as the working electrodes, Ag/AgCl/3M KCl (RE-5B, Bioanalytical Systems, Inc., IN, USA) and a platinum wire served as the reference and auxiliary electrodes, respectively. The use of an aqueous reference electrode for measurement in non-aqueous electrolytes was justified by recording the cyclic voltammogram of ferrocene. The GC plates and ITO glass slides were connected to a potentiostat with the aid of a copper tape with a conductive (0.005 Ohm cm⁻¹) adhesive. The tape (CU TAPE SA 1M/6MM, GES electronic, Czech Republic) was placed along the entire length of the upper edge of the plate/slide. The electrochemical experiments were done from a solution of the given helicene (1 mM) in acetonitrile/0.1 M tetrabutylammonium perchlorate (ACN/0.1 M TBAP) or Britton-Robinson Buffer (pH 7.4). All electrochemical data were evaluated using the freeware package eL-Chem Viewer ¹⁰.

Scanning electron microscopy (SEM) images were obtained with a Tescan Vega 3 (SE image resolution 2 nm at 30 kV). The images were collected with a high voltage of 10 kV at a working distance ranging from 5 mm to 25 mm. The sample material was immobilized onto conductive carbon discs. For other details see ref. ⁶.

The structures of the studied molecules were optimized using density functional theory (DFT) with the hybrid three-parameter Becke–Lee–Yang–Parr (B3LYP) functional ^{11,12} and with the 6-311++G** basis set. Acetonitrile solvent in the DFT calculations was simulated with the polarizable continuum model (PCM). A vibrational analysis was carried out for each structure in order to confirm whether it corresponded to a minimum on the potential energy surface. Other details can be found in ref. ⁷.

Results and Discussion

In this contribution we deal with the electrochemical characterization of helical polyaromatics, specifically the anodic reactions of helicenes **1-3** and their two conjugates **4,5** (Fig. 1). At first, the redox transformations of **1-3** were investigated. These substances are water-insoluble, therefore acetonitrile (ACN) supported with 0.1 M TBAP was used in the studies of their oxidation. CV analyses were carried out on the GCE at 23 °C in the presence of oxygen. The obtained voltammograms (Fig. 2A) indicate complex (multi-step) anodic reactions, distinct for each helicene in the study.

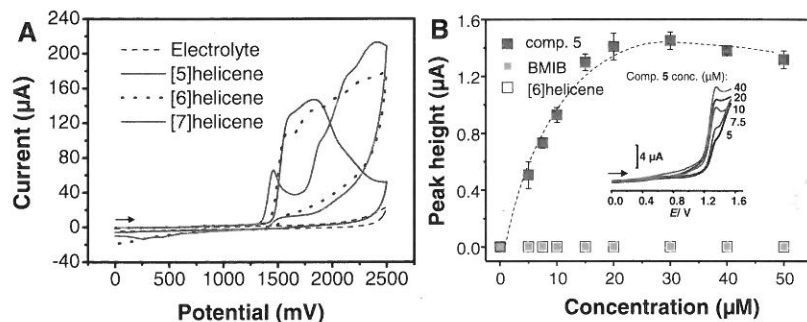


Fig. 2. (A) Cyclic voltammograms of 1 mM $[n]$ helicenes in 0.1 M TBAP/ACN, scan rate 100 mV/s, initial potential 0 V. (B) Dependence of SWV response on concentration of **5**, BMIB and $[6]$ helicene. Inset: SW voltammograms of **5** in concentration range from 5 to 40 μM . All compounds were first solubilized in DMSO and then dissolved in the supporting electrolyte (Britton-Robinson buffer, pH 7.4) where SWV analyses were performed. GCE vs. Ag/AgCl/3M KCl and air-saturated electrolytes were used for both A and B.

Under the given experimental conditions, the anodic reactions correspond to diffusion-driven processes. It is expected that $[n]$ helicenes are subject to electrochemical transformations similar to those described previously for planar polyaromatics ¹³. The resulting oxidation products are oxygen-containing helicene derivatives, as confirmed by MS analyses of electrolytes (not shown). During repeated anodization of the electrode immersed in 1 mM helicene solution, a decrease in CV peak height was observed, indicating the passivation of the electrode surface and formation of a polymeric deposit on the GCE. This behavior was observed for all the studied helicenes **1-3**. The aforementioned polymeric layers were

prepared on the ITO electrode and subjected to spectroscopic and microscopic (SEM) characterization according to the methodology given in ⁸. It has been confirmed that it is possible to fabricate thin helicene films on conductive substrates this way. The aim here is to deposit compact layers with semiconducting properties which would find applications in optoelectronics and in the field of spectroelectrochemical sensing. The electronic properties of helicene monomers were studied by a computational chemistry method (DFT) ⁷, complementary to the above-described electrochemical experiments.

Polymer structures capable of transporting electrons (tunneling effects) or functional organic semiconducting layers can be prepared using electrochemical approaches. Accordingly a hybrid substance **4** was prepared, composed of $[7]$ helicene and thiophene, a known electropolymerizable monomer ^{14,15}. Conjugate **4** undergoes electrochemical oxidation under identical conditions to those described in the previous paragraph, with the difference that not only $[7]$ helicene but also the thiophene moiety is involved in the polymerization process. Semiconductive as well as overoxidised layers can be prepared on GC and carbon fiber electrodes this way ⁶. By the judicious selection of electrosynthesis conditions, the physicochemical properties (e.g. thickness and porosity) of the resulting deposit can be controlled.

As was mentioned above, substances **1-4** are insoluble in aqueous solvents or electrolytes, which can be a limitation for certain immobilization procedures or applications (e.g. in biosensing). For this reason the conjugate of helicene with imidazolium bromide **5** was prepared. The compound can be oxidized in an aqueous environment, as evidenced by a comparative square-wave voltammetric (SWV) analysis of **5** and its structural components, i.e. BMIB (1-butyl-3-methylimidazolium bromide) and $[6]$ helicene in Britton-Robinson buffer (Fig. 2B). Its partial solubility in an aqueous environment enables compound **5** to be applied in the research of biomolecular interactions – e.g., a positive charge in the molecule increases its affinity to the negatively charged structures of nucleic acids (not shown). The increased solubility in polar solvents also facilitates some surface immobilization techniques. Compound **5** was immobilized onto non-conductive substrates by spincoating, the electronic components prepared in this way exhibited unique conductivity parameters and were applied as experimental humidity sensors ⁷.

Until now, only racemic samples of polyaromatics **1-5** were studied. For this reason synthetic or chiral separation procedures were developed enabling optically pure $[n]$ helicenes to be obtained, e.g. compound **5** was recently prepared in the form of optically pure P and M enantiomers (Fig. 1). Their chirality and specific optical activity together with their conductivity grant the studied $[n]$ helicenes and their derivatives broad application potential in the preparation of chiroptic materials and spectroelectrochemistry. The technique used to immobilize helical polyaromatics onto solid supports plays a key role in their applicability. In this field, anodic electropolymerization procedures could be a promising method.

Conclusion

In this short contribution we presented the experimental characterization of $[n]$ helicenes and their hybrids composed of a helicene moiety (conjugated helical system) and thiophene (polymer forming system) or imidazolium (solubilization and surface immobilization system). In addition to characterizing $[n]$ helicene monomers, we applied a spincoating strategy and electropolymerization approaches for the preparation of polymeric films and thin layers with electron transfer properties ^{6,7}. These results will serve as the basis for further applications of

the new helicene-based derivatives and polymers or composites for the preparation of semiconductive devices and the development of advanced optoelectronics instruments.

Acknowledgement

This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic, COST Action EU-ROS, BM1203 (project No. LD14033) and by the Institutional Funding from Palacky University (IGA_LF_2016_012).

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Voltammetric Determination of Acrylamide in Food (Voltammetrické stanovení akrylamidu v potravinách)

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Abstract

The new voltammetric procedure has been used for determination of acrylamide in food. It was found that the complex of acrylamide and Ni²⁺ was suitable for electrochemical determination of acrylamide. Voltammetric measurements were done on polarographic equipment in three-electrode configuration with hanging mercury drop electrode as the working electrode. Peak heights were a function of acrylamide concentrations and deposition time. Sample preparation procedure was optimized. The accuracy of the method was verified by use of standard reference materials. Contents of acrylamide were analyzed in different brands of foodstuff.

Key words: Acrylamide, Electrochemistry, Foodstuff, Nickel, Adsorptive stripping voltammetry, Endogenous contaminant.

Úvod

Akrylamid (prop-2-enamid; C₃H₅NO) je organický amid kyseliny akrylové, za běžných podmínek bílá krystalická látka dobře rozpustná v polárních rozpouštědlech. Průmyslově vyráběný akrylamid se běžně používá k výrobě polyakrylamidu. Monomer i polymer nalézají uplatnění v papírenském, metalurgickém a textilním průmyslu, ve stavebnictví, při výrobě plastických hmot a kosmetiky, barviv a lepidel. Polymer je využíván flokulant při úpravě pitné vody. Akrylamidový gel se používá při elektroforéze v laboratořích. Jeho přítomnost byla prokázána v cigaretovém kouři ¹.

Akrylamid (AA) je neurotoxická, mutagenní a genotoxická látka. U laboratorních zvířat jsou prokázány karcinogenní účinky a poruchy reprodukce ^{2,3}. Podle Mezinárodní agentury pro výzkum karcinogenity (IARC) je akrylamid zařazen do skupiny 2A (pravděpodobně karcinogenní pro člověka) ⁴. V roce 2002 byla prokázána přítomnost akrylamidu v potravinách a byl zařazen mezi endogenní kontaminanty potravin. V potravinách a krmivech vzniká přirozeně reakcí mezi NH₂- skupinou asparaginu s karbonylovou skupinou redukujícího cukru jako součást tzv. Maillardovy reakce ⁵. Běžně je stanovován v potravinách bohatých na škroby, které byly tepelně upravovány při teplotách vyšších než 120 °C, což zahrnuje technologické úpravy jako je smažení, pečení, pražení nebo grilování. Nejvyšší obsah akrylamidu byl stanoven v bramborových lupíncích a hranolcích. Dále v sušenkách, snídanových cereáliích, pečivu a kávě. V syrových nebo vařených potravinách nebyla přítomnost akrylamidu prokázána ^{6,7}.

Ke stanovení akrylamidu v potravinách se běžně plynová chromatografie s hmotnostní spektrometrií (GC-MS) nebo vysokoúčinná kapalinová chromatografie s hmotnostní spektrometrií (LC-MS/MS). Výhodou těchto metod je jednoduché a rychlé provedení analýzy a potřeba malého množství vzorku. Nevýhodou je delší doba přípravy vzorku při některých