

STRESZCZENIE W JĘZYKU ANGIELSKIM

The properties of (hetero)acenephosphonates, especially tricyclic anthracenephosphonates and higher analogues, remain insufficiently studied and characterized. This mainly applies to systems with a high degree of substitution in the aromatic ring. The literature provides only limited information on their properties, especially in the context of research on new functional materials. Most existing methods for the synthesis of acenephosphonates focus on obtaining the simplest derivatives of this group of compounds. Furthermore, most of the reported examples involve procedures requiring harsh reaction conditions, which limit the efficient synthesis of more complex systems containing thermally sensitive substituents.

Therefore, the research conducted as part of this dissertation aimed to develop a suitable method for the synthesis of multiply substituted dialkyl (hetero)acenephosphonates, thereby filling the existing gaps in the literature. This aim was achieved through a four-step procedure, the key element of which was the development of a new *phospho*-Friedel-Crafts-Bradsher cyclization converting diarylmethylphosphonates into dialkyl 10-anthracenephosphonates. As a result of this synthesis, 17 new dialkyl (dimethyl, diethyl, diisopropyl) 10-(hetero)anthracenephosphonates were obtained in yields ranging from 70 % to 97 %. A significant advantage of the method was that mild reaction conditions were maintained at each stage, enabling the synthesis of acenes substituted with functional groups exhibiting diverse thermal and photochemical stabilities as well as electronic properties.

The obtained dialkyl (dimethyl, diethyl) 10-anthracenephosphonates were employed for the synthesis of acenephosphonic acid monoesters, acids, and dithioesters. Acenephosphonic acid monoesters were prepared *via* reaction of the esters with LiBr, while acenephosphonic acids were obtained by transesterification of the dialkyl esters with trimethylsilyl bromide followed by hydrolysis of the resulting bis(trimethylsilyl) esters. Furthermore, a three-step, *quasi*-one-pot procedure was developed for the synthesis of anthracenephosphonic acid dithioesters, yielding 10 new analogues.

Attempts to incorporate lanthanide ions (La^{3+} , Tb^{3+} , Eu^{3+} , Gd^{3+}) into the obtained monoesters, phosphonic acids, and phosphonates did not yield fluorescent complexes due to the strong tendency of these molecules to aggregate, resulting in practically insoluble solids.

Investigations to replace the bromine atom at position 7 of the anthracenephosphonate ring with the phenylacetylene group *via* the Sonogashira coupling to achieve π -expansion of the aromatic system were successful for 7-bromo-6-formylanthracene, whereas the 7-bromoanthracene derivative lacking a CHO group did not yield the expected product.

The obtained 10-(hetero)acenephosphonates and their derivatives were subjected to photophysical studies, including UV absorption, photoluminescence and photoluminescence quantum yield (PLQY) measurements. Chemical calculations were carried out using DFT and TD-DFT/B3LYP/6-311++G(d,p) methods (*density functional theory*, DFT) to investigate ground and excited states. Additionally, IFCT (*Inter-fragment Charge Transfer*) analysis was performed to evaluate the contribution of charge transfer (CT) to the excitation mechanism.

Based on the studies conducted, it was found that the obtained diesters and dithioesters exhibited very high quantum yields (PLQY), up to 99.2 %, and large Stokes shifts, up to 8088 cm⁻¹. Furthermore, the introduction of substituents with different electronic characteristics into the acene core and the modification of the phosphonate group in 10-anthracenephosphonates affected not only the PLQY and Stokes shifts of individual systems, but also their emission maxima.