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Photochromism of dihydroindolizines. Part XVI: first attempts toward molecular wires comprising photochromic dihydro 5-azaindolizines and π-extended ethynyl and butadiynyl oxadiazole derivatives

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ABSTRACT

Eight new photochromic dihydro 5-azaindolizines (DHAIs) linked with 2,5-diaryl-1,3,4-oxadiazole (OXD) derivatives containing terminal ethynes and butadiyne substituents on the fluorene part of the DHAI skeleton are synthesized via palladium-mediated coupling reaction pathways. Irradiation of the DHAI-OXD derivatives with polychromatic light affords red- and green-colored betaines.

Recently, there has been a renaissance in the chemistry of aromatic alkynes utilizing the palladium-catalyzed cross-coupling reactions of terminal alkynes with aryl halides (the Sonogashira reaction).[1] This protocol provides an efficient and versatile means of extending π–π conjugation in organic compounds, affording simplified molecular structures compared with their alkene analogues which exhibit *Z*/*E* isomerism. Ethynylene-extended arenes and heteroarenes have been shown to function as nanoscale ‘molecular wires’, with the extent of intramolecular conjugation dependent upon the topology of the π-system and the molecular length.[2] Synthetic advances have led to remarkable polyene systems of nanoscale lengths end-capped with organometallic[3] or silyl substituents.[4] However, ethyne and butadiyne derivatives remain fundamentally important targets for studies on optoelectronic properties of carbon-rich backbones which have not been well-established experimentally. In this context, Wang et al.[5,6] studied 2,5-diaryl-1,3,4-oxadiazole (OXD) derivatives due to their good thermal and chemical stabilities and their high photoluminescence quantum yields. Photochromic dihydroindolizines (DHIs) and dihydro 5-azaindolizines (DHAIs), which were discovered and developed by Dürr,[7] are well-known photochromic materials that have attracted significant interest from the viewpoints of both fundamental elucidation of electrocyclization reactions and their potential applications to optical memories and switches.[8] These materials, based on the 1,5-electrocyclization between two distinct isomeric states: ring-opened form (betaine-form) and ring-closed form (DHI or DHAI forms), are promising candidates for optical storage media and electronic devices.[9] In continuation of our research on the synthesis and photochromic properties of active functionalized systems suitable for molecular wires and electronic device applications, the aim of the present work was to develop the synthetic chemistry of photochromic dihydro 5-azaindolizines bearing OXD-derivatives possessing terminal ethynyl and butadiyne substituents on the fluorene part of the DHAI skeleton.[6,9] The synthesis of the target molecules through various Sonogashira-mediated coupling reactions is described.

2,5-Diaryl-1,3,4-oxadiazole derivatives **1** and **2a**,**b** were synthesized according to the established procedures.[6] The synthesis of spirocyclopropenes **8a**–**d** was accomplished in five steps, starting with the previously known conversion of fluorenone into 2-mono and 2,7-diiodo-9*H*-fluoren-9-one in 54% yield in three steps[9] (Scheme 1). The Sonogashira coupling of 2-mono and 2,7-diiodo-9*H*-fluoren-9-ones **3a**,**b** with 2-(4-*tert*-butylphenyl)-5-(4-ethynylphenyl)-1,3,4-oxadiazole **2a** (OXD1) and 2-[4-(buta-1,3-diynyl)phenyl]-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **2b** (OXD2) in the presence of $Pd(PPh_3)_2Cl_2/Cu_2I_2/Et_3N$ in THF at 45 °C for 12 h afforded the coupled products **4a**–**d** in moderate yields (46–59%).

Condensation of **4a**–**d** with anhydrous hydrazine in boiling ethanol for 4 h led to the formation of the corresponding hydrazones **5a**–**d** in excellent yields (86–94%). The evidence for the formation of compounds **5** was provided by ^1H NMR spectra which showed a

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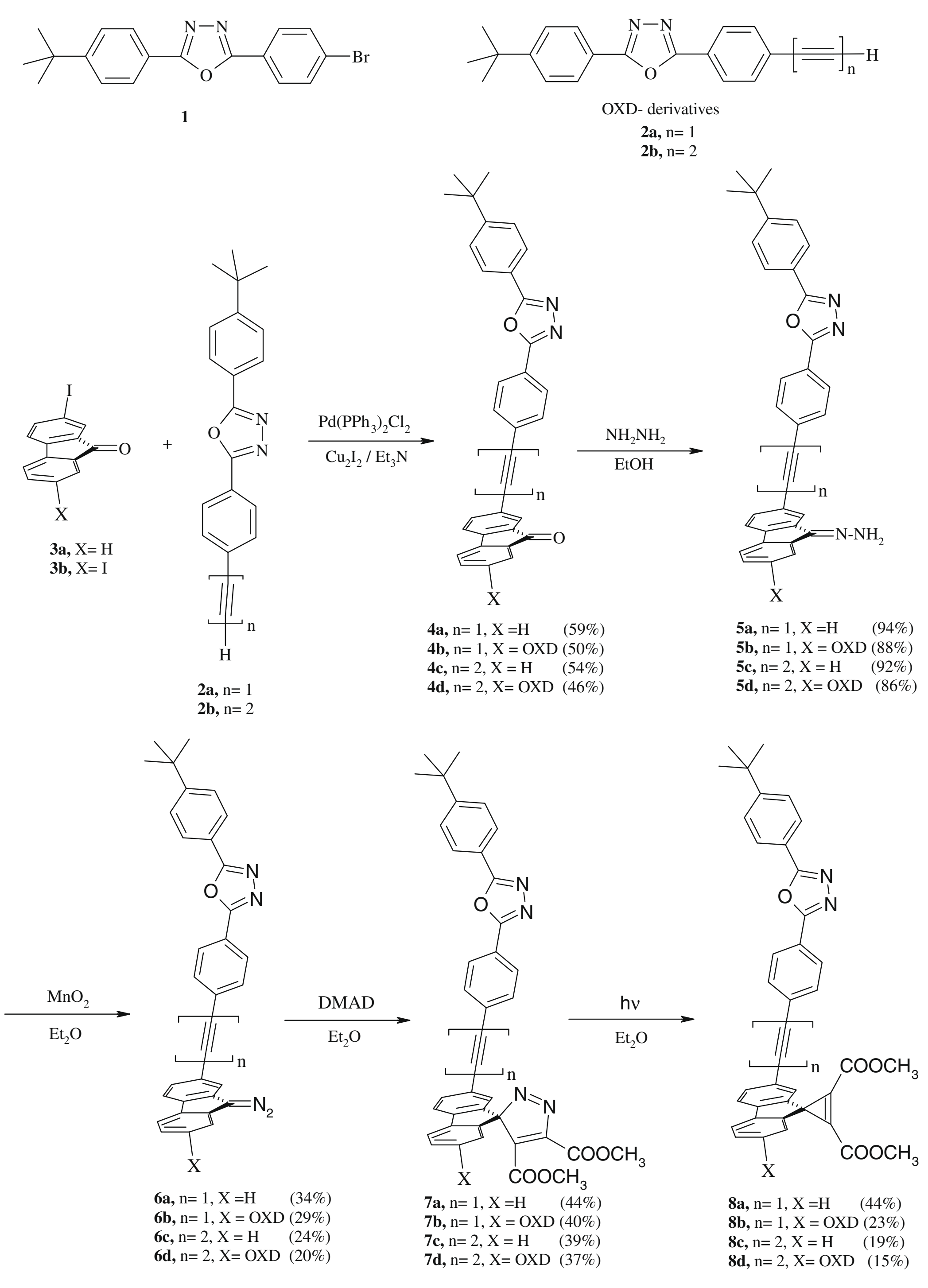
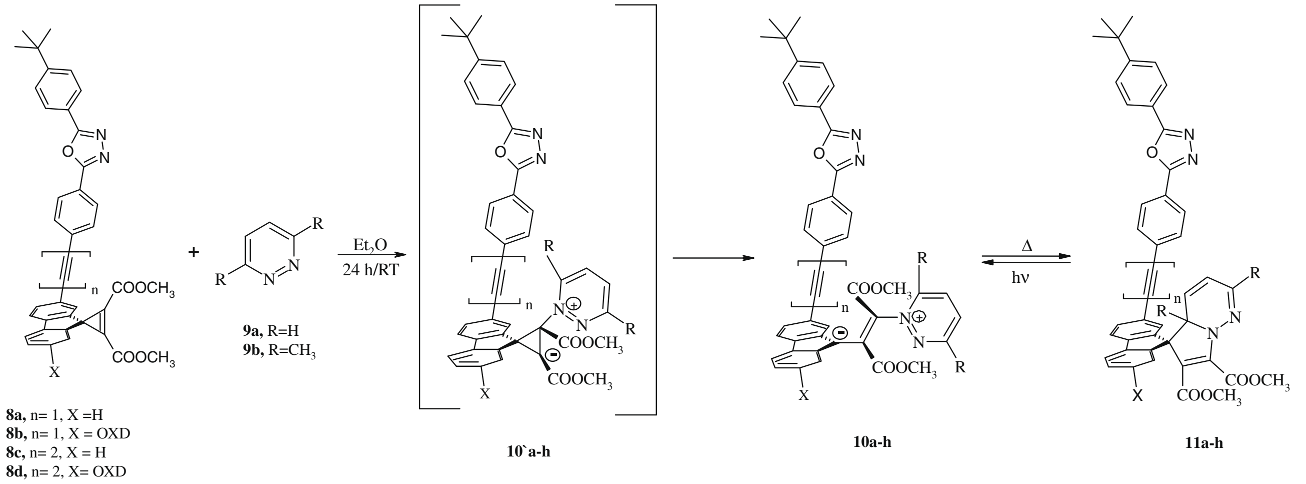


Scheme 1. Preparation of mono- and disubstituted spirocyclopropene-OXD precursors **8a–d**.

broad singlet at 4.98–5.08 ppm corresponding to the NH_2 protons which disappeared upon treatment with deuterium oxide. Also, the IR spectra showed that the carbonyl absorptions present in compounds **4** at 1712–1727 cm^{-1} had disappeared and instead, amino group absorptions at 3200–3220 cm^{-1} were detected. Oxidation of the hydrazones **5a–d** with manganese dioxide in dry ether at room temperature in the absence of light for 9 h afforded the 9-diazo-derivatives **6a–d** in poor yields (20–34%). Reaction of dimethyl acetylenedicarboxylate (DMAD) with the 9-diazofluorene derivatives **6a–d** in dry ether in the dark for 12 h led to the formation of pyrazole cycloadducts **7a–d** in 37–44% yields. The spirocyclopropene precursors **8a–d** were obtained via photolysis of pyrazoles **7a–c**. The photolysis was carried out using a high pressure mercury lamp (125 W) in dry ether solution for 3 h under a nitrogen atmosphere.

Pure spirocyclopropene derivatives **8a–d** were obtained in low yields (15–28%) after flash chromatography purifications. The low yields can be attributed to the formation of unidentified byproducts which may be derived from addition polymerization on the acetylenic groups in the fluorene part. The structures of the newly synthesized spirocyclopropenes **8a–d** (Scheme 1) were established by spectroscopy (NMR, IR, and mass spectrometry)

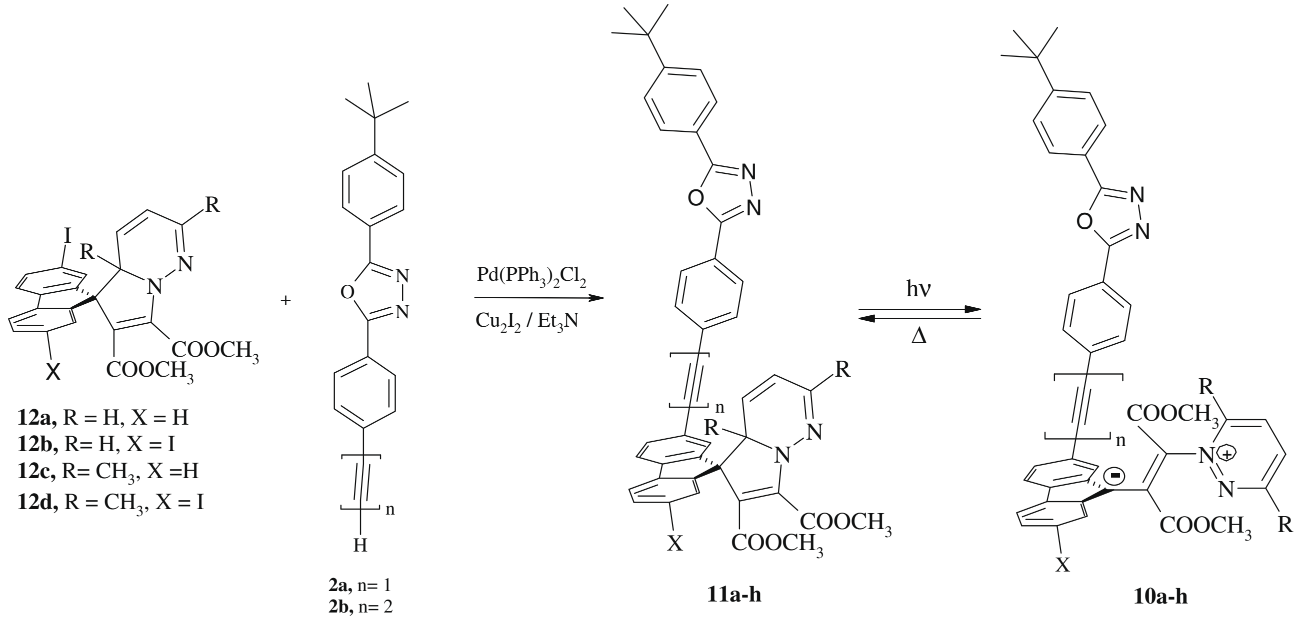


Scheme 2. Preparation of photochromic DHAIs **11a–h** (method A) from spirocyclopropenes **8a–d** (**11a**, R = X = H, *n* = 1; **11b**, R = X = H, *n* = 2; **11c**, R = H, X = OXD, *n* = 1; **11d**, R = H, X = OXD, *n* = 2; **11e**, R = CH_3, X = H, *n* = 1; **11f**, R = CH_3, X = H, *n* = 2; **11g**, R = CH_3, X = OXD, *n* = 1; **11h**, R = CH_3, X = OXD, *n* = 2).

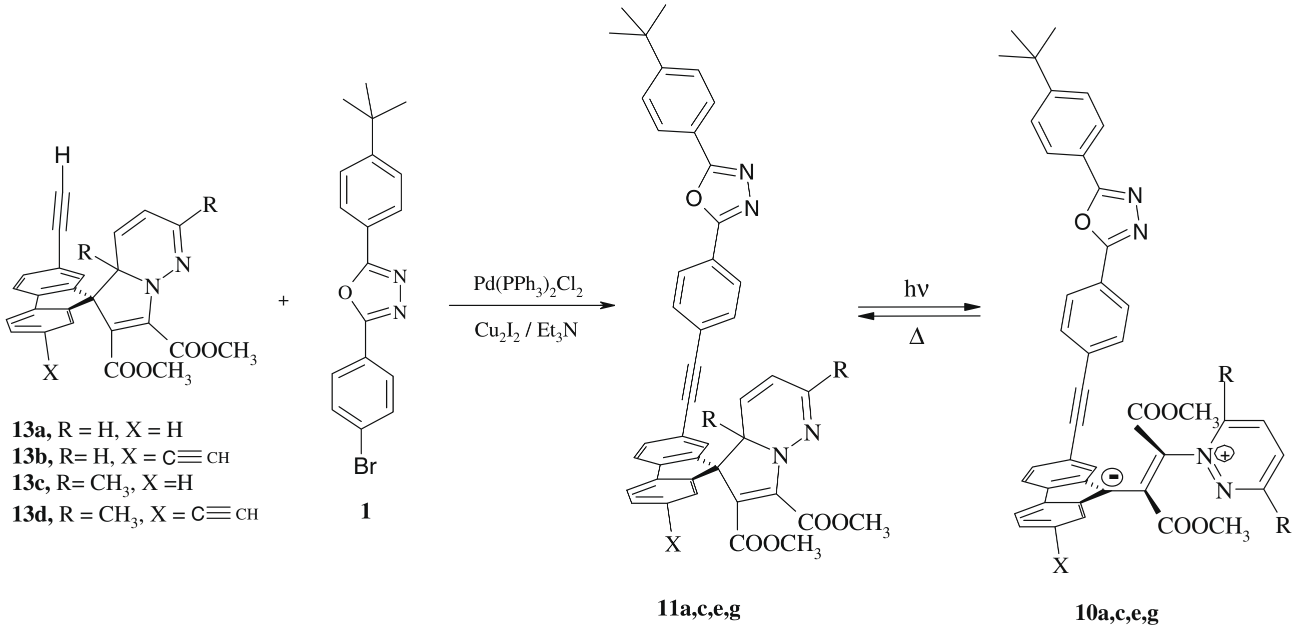
and elemental analysis data. For example, the ^{1}H NMR (400 MHz, $CDCl_3$) of spirocyclopropene precursor **8c** showed the following signals: δ 8.45 (d, *J* = 7.8 Hz, 2H, CH-arom), 8.33 (d, *J* = 7.8 Hz, 1H, CH-arom), 8.01 (d, *J* = 7.8 Hz, 1H, CH-arom), 7.92 (d, *J* = 7.8 Hz, 2H, CH-arom), 7.73 (s, 1H, CH-arom), 7.57 (d, *J* = 7.8 Hz, 2H, CH-arom), 7.42 (d, *J* = 7.8 Hz, 2H, CH-arom), 7.34 (d, *J* = 7.8 Hz, 1H, CH-arom), 7.30 (t, *J* = 6.7, 2H, CH-arom), 7.20 (t, *J* = 6.7, 1H, CH-arom), 3.81 (s, 6H, 2′, 3′-CH_3), 1.31 [s, 9H, $C(CH_3)_3$] ppm.

Electrophilic addition of spirocyclopropenes **8a–d** to pyridazine **9a** and 2,6-dimethylpyridazine **9b** using the cyclopropene route[8,9] (Scheme 2) in dry ether at room temperature under dry nitrogen in the absence of light for 12 h (TLC monitoring using CH_2Cl_2 as eluent) led to the formation of the photochromic dihydro 5-azaindolizines (DHAIs) **11a–h** in poor yields (18–29%, method A and Table 1 in the Supplementary data). The formation of the photochromic DHAIs **11a–h** occurs through electrophilic addition of the electron-deficient spirocyclopropenes **8a–d** to the nitrogen of the pyridazines **9a**,**b** which led to the ring-opening via a cyclopropyl-allyl conversion **10′a–h** to the colored betaines **10a–h**. Subsequent ring-closure to DHAIs **11a–h** occurred via a slow thermal 1,5-electrocyclization reaction which can be reversed upon exposure to light.

Photochromic DHAIs **11a–h** were obtained in a pure form by column chromatography on silica gel using dichloromethane as the eluent. An alternative successful method for the synthesis of the target photochromic DHAIs **11a–h** (Scheme 3) was achieved through the palladium-mediated Sonogashira coupling of (5′*R*)-dimethyl 2-iodo- and 2,7-diiodo-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-*b*]pyridazine]-6′,7′-dicarboxylates **12a**,**b** and (5′*R*)-dimethyl 2-iodo- and 2,7-diiodo-2′,4a′-dimethyl-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-*b*]-pyridazine]-6′,7′-dicarboxylates **12c**,**d** which were previously prepared by us,[9g,h] with OXD-derivatives **2a**,**b**. The palladium-catalyzed reaction (2.5% or 5%, for mono- and di-OXD derivatives, respectively) in the presence of Cu_2I_2/Et_3N in dry THF for 8 h yielded the desired photochromic-OXD systems **11a–h** in moderate yields (38–53%) after purification by flash column chromatography on silica gel using CH_2Cl_2 as eluent (method B, Supplementary data).



Scheme 3. An alternative pathway (method B) for the synthesis of photochromic DHAIs **11a–h** (**11a**, R = X = H, *n* = 1; **11b**, R = X = H, *n* = 2; **11c**, R = H, X = OXD, *n* = 1; **11d**, R = H, X = OXD, *n* = 2; **11e**, R = CH_3, X = H, *n* = 1; **11f**, R = CH_3, X = H, *n* = 2; **11g**, R = CH_3, X = OXD, *n* = 1; **11h**, R = CH_3, X = OXD, *n* = 2).



Scheme 4. An alternative pathway (method C) for the synthesis of photochromic DHAIs **11a**,**c**,**e**,**g** (**11a**, R = X = H, *n* = 1; **11c**, R = H, X = OXD, *n* = 1; **11e**, R = CH_3, X = H, *n* = 1; **11g**, R = CH_3, X = OXD, *n* = 1).

In addition, photochromic DHAIs-OXD **11a**,**c**,**e**,**g** were successfully synthesized via Sonogashira-mediated coupling of dimethyl 2- or 2,7-ethynyl-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-*b*]pyridazine]-6′,7′-dicarboxylates **13a**,**b** and dimethyl 2- or 2,7-ethynyl-2′,4a′-dimethyl-4a′*H*-spiro[fluorene-9,5′-pyrrolo[1,2-*b*] pyridazine]-6′,7′-dicarboxylates **13c**,**d** with 2-(4-bromophenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole **1**. The palladium-catalyzed reaction (2.5% or 5%, for mono- and di-OXD derivatives, respectively) with Cu_2I_2/Et_3N in dry THF for 5 h yielded the desired photochromic-OXDs in good yields (31–46%) after purification by flash column chromatography on silica gel using CH_2Cl_2 as eluent (Scheme 4, method C, Supplementary data). The obtained products from the three different pathways gave the same analytical and spectroscopic data as well as the same melting points (see Table 1 in the Supplementary data).

Irradiation of photochromic DHAI-OXD derivatives **11a**–**h** with polychromatic light in CH_2Cl_2 afforded red-colored betaines **10a**–**d** and green–blue colored betaines **11e**–**h**. Details on the photochromic properties, fluorescence, and photoluminescence will be described in detail in a forthcoming paper.

In conclusion, photochromic dihydro 5-azaindolizines (DHAIs) incorporating 2,5-diphenyl-1,3,4-oxadiazole (OXD) derivatives containing terminal ethynyl- and butadiyne substituents on the fluorene part of the DHAI skeleton have been synthesized using three reaction pathways following Sonogashira-mediated coupling methodologies. The three synthetic procedures gave identical products as was proved by both analytical and spectroscopic methods. In addition, new spirocyclo-propenes containing OXD systems have been synthesized via chemical and photochemical procedures.

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Supplementary data

Supplementary data (synthetic procedures and analytical and spectroscopic characterization) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2009.11.117.

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