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Synthesis of new pyrazolyl-1,3-diazabicyclo[3.1.0]hexe-3-ene derivatives

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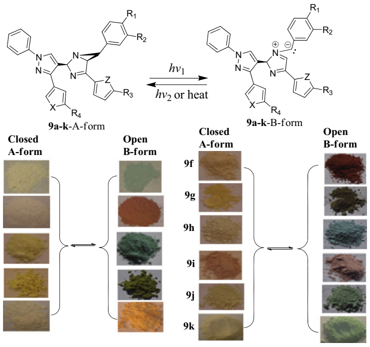
HIGHLIGHTS

- A series of 1,3-diazabicyclo[3.1.0]hex-3-enes containing pyrazole moiety have been prepared.
- The structures characterized by IR, ^{1}H NMR, ^{13}C NMR, and UV–Vis spectra.
- Photochromic behavior in the both solid and solution phases.
- 1,3-Diazabicyclo[3.1.0]hex-3-enes containing thiophene fragment have been synthesized.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of new of photochromic 1,3-diazabicyclo[3.1.0]hex-3-ene derivatives based on the skeleton of five-membered pyrazole moiety have been synthesized and characterized by spectral techniques, as well as their photochromic properties were examined under UV light irradiation in various solutions. All these newly synthesized compounds showed good photochromic properties in the both solution and solid states. The UV–Visible spectral analysis of the corresponding pyrazolyl bicyclic aziridines established structure-photochromic behavior relationships.

Introduction

Molecules that exhibit reversible, light-induced transformations between two isomers with different absorption spectra are called photochromes and the related phenomenon is known as photochromism [1,2]. This phenomenon provides an appropriate approach to the development of light-sensitive eyewear [2], high-density optical memory [3], molecular photonic devices [4], optical sensing applications [5], and photo-switches [6]. Polyaromatic bicyclic aziridine derivatives constitute an interesting class of organic photochromic compounds have special photochromic properties. These intelligent photochromes display the noticeable color change as a result of the photochromic reaction in the both solid and solution phases. This property lets us to study them as nominees in the exploration for intelligent photochromic materials. The photochromism of 1,3-diazabicyclo[3.1.0]hex-3-enes is attributable to the reversible photochemical cleavage of the C—N bond in the aziridine unit, which leads to the relatively longer π-conjugation in the colored isomer (a zwitterion species) and thus shifts the absorption to the visible region [7–45].

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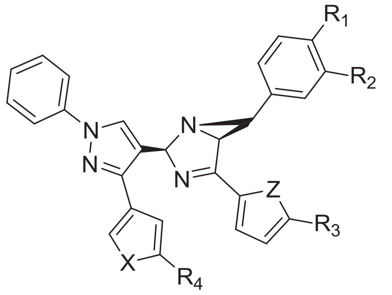
Pyrazoles, on the other hand, are well-known examples of double nitrogen-containing heterocyclic aromatic organic compounds accompanying with interesting pharmaceutical properties in medicinal chemistry as well as useful intermediates in synthetic organic chemistry. Compounds containing pyrazole ring and their derivatives often exhibit a wide range of physiological and pharmacological activities, such as anti-inflammatory [46], antibacterial [47], anticonvulsant [48], anticancer [49], anti-hyperglycemic [50], antipyretic [51], antioxidant [52], antitubercular [53], fungicides [54], and analgesic [55]. These heterocycles have also found applications in transition-metal chemistry as an analytical reagent [56] as well as are often used as antioxidant additives to fuels [57]. Moreover, some pyrazole-containing compounds are used as ligands for the transition-metal-catalyzed cross-coupling reactions [58,59]. As a great deal of interest has been focused on them, we synthesized some new pyrazolyl bicyclic aziridinyl compounds. In the present work, at first we synthesized with the aim of building new pyrazole-containing polyaromatic bicyclic aziridines and its manipulation, as shown in Fig. 1.

Experimental

General

Melting points were measured on a Buchi 510 melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at ambient temperature on a Bruker AVANCE DRX-500 and 400 MHz using $CDCl_3$. FT-IR spectra were recorded on a Perkin–Elmer RXI spectrometer. UV spectra were recorded using Analytik Jena UV/Vis spectrometer (Specord 205) or Perkin-Elmer Lambda spectrophotometer. The photoinduced (open) form was formed upon UV irradiation (Hg lamp DRSh-260+UV-transmitting glass filters). Chemicals were obtained from Merck and Fluka. Solvents were dried by standard methods. The development of reactions was monitored by thin layer chromatography (TLC) analysis on silica gel 60 GF_{254} aluminium sheets, using ethyl acetate: petroleum ether or hexane as mobile phase. The spots were exposed by UV light.



9a: $R_1 = NO_2$, $R_2 = R_3 = R_4 = H$, Z = X = (CH=CH)
9b: $R_1 = R_3 = R_4 = H$, $R_2 = NO_2$, Z = X = (CH=CH)
9c: $R_1 = NO_2$, $R_2 = R_4 = H$, $R_3 = 4\text{-}OCH_3$, Z = X = (CH=CH)
9d: $R_1 = NO_2$, $R_2 = R_3 = H$, $R_4 = Cl$, Z = X = (CH=CH)
9e: $R_1 = R_3 = H$, $R_2 = NO_2$, $R_4 = Cl$, Z = X = (CH=CH)
9f: $R_1 = NO_2$, $R_2 = H$, $R_3 = R_4 = 4\text{-}OCH_3$, Z = X = (CH=CH)
9g: $R_1 = R_4 = NO_2$, $R_2 = R_3 = H$, Z = X = (CH=CH)
9h: $R_1 = NO_2$, $R_2 = R_3 = R_4 = H$, Z = (CH=CH), X = S
9i: $R_1 = R_3 = R_4 = H$, $R_2 = NO_2$, Z = (CH=CH), X = S
9j: $R_1 = NO_2$, $R_2 = R_3 = H$, $R_4 = 4\text{-}OCH_3$, Z = S, X = (CH=CH)
9k: $R_1 = NO_2$, $R_2 = R_4 = H$, $R_3 = 4\text{-}OCH_3$, Z = (CH=CH), X = S

Fig. 1. Structures of photochromic pyrazolyl bicyclic aziridines **9a–k.**

*General procedure for the synthesis of target compounds **9a–k***

To a magnetically stirred solution of 1 mmol of *trans*-ketoaziridine **4** and 1 mmol of 1-phenyl-3-arylpyrazole-4-carbaldehyde **8** in 7 mL of absolute ethanol was added NH_4OAc (0.78 g, 10 mmol) at room temperature. The reaction mixture was stirred for specified time. The solvent from the mixture was evaporated under reduced pressure to leave a residue that was washed with absolute ethanol, dried under vacuum, and the resulting solid was recovered, purified by silica gel column chromatography using ethyl acetate: hexane (1:3, v/v) as the eluent, and recrystallized from absolute ethanol (10 mL) to afford the target compounds **9a**–**k**. Spectral data are listed below.

*2-(1,3-Diphenyl-1H-pyrazol-4-yl)-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**9a**)*

Yield: 82%; m.p. 145–146 °C; as a beige solid; IR (KBr, cm^{-1}): 3073, 1599, 1549, 1513, 1450, 1342, 1218, 1022, 958, 860, 817, 773, 695; (closed-form, 38%) ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.73 (s, 1H, H-6), 3.74 (s, 1H, H-5), 6.86 (s, 1H, H-2), 7.30–7.51 (m, 7H), 7.55–7.57 (m, 2H), 7.60–7.66 (m, 2H), 7.79–7.81 (m, 2H), 7.99 (s, 1H, H-pyrazole), 8.02–8.05 (m, 2H), 8.11 (d, $J = 8.0$ Hz, 2H), 8.18 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.3 (C-6), 58.2 (C-5), 90.3 (C-2), 119.5, 119.7, 122.7, 123.9, 126.9, 127.9, 128.0, 131.8, 132.4, 133.6, 140.4, 145.4, 147.1, 147.9, 171.6 (C-4); after irradiation with UV light converted to green (open-form: 62%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.87 (d, $J = 1.4$ Hz, 1H, H-6′), 3.83 (t, $J = 2.3$ Hz, 1H, H-5′), 6.40 (d, $J = 2.7$ Hz, 1H, H-2′), 7.30–7.51 (m, 7H), 7.55–7.57 (m, 2H), 7.60–7.66 (m, 2H), 7.79–7.81 (m, 2H), 7.95 (s, 1H, H-pyrazole′), 8.02–8.05 (m, 2H), 8.11 (d, $J = 8$ Hz, 2H), 8.25 (d, $J = 8.6$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 48.6 (C-6′), 57.3 (C-5′), 91.5 (C-2′), 119.3, 119.7, 122.7, 124.2, 127.0, 127.3, 127.7, 131.8, 132.4, 133.3, 140.5, 145.5, 147.9, 151.2, 151.5, 170.2 (C-4′); UV/Vis (EtOH) λ_{max}/nm: 269 before irradiation and 269, 410 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 280 before irradiation and 280, 420 nm after irradiation.

*2-(1,3-Diphenyl-1H-pyrazol-4-yl)-6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**9b**)*

Yield: 85%; m.p. 176–178 °C; as a colorless solid; IR (KBr, cm^{-1}): 3061, 1598, 1529, 1500, 1450, 1350, 1213, 1046, 958, 907, 875, 771, 691; (closed-form, 72%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.74 (s, 1H, H-6), 3.75 (s, 1H, H-5), 6.87 (s, 1H, H-2), 7.32 (d, $J = 1$H, 1H), 7.40–7.62 (m, 9H), 7.79–7.83 (m, 2H), 7.97 (s, 1H, H-pyrazole), 8.02–8.13 (m, 5H), 8.19 (d, $J = 7.3$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 42.0 (C-6), 58.0 (C-5), 90.3 (C-2), 119.0, 119.2, 122.0, 122.7, 129.0, 127.3, 128.0, 128.5–129.8 (8 C Ar), 132.0, 132.3, 133.1, 140.2, 148.7, 151.2, 171.4 (C-4); after irradiation with UV light converted to deep orange (open-form, 28%): ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.88 (s, 1H, H-6′), 3.85 (s, 1H, H-5′), 6.41 (d, $J = 2.28$ Hz, 1H, H-2′), 7.32 (t, $J = 6.25$ Hz, 1H), 7.40–7.62 (m, 9H), 7.79–7.83 (m, 2H), 7.97 (s, 1H, H-pyrazole’), 8.02–8.13 (m, 4H), 8.19 (d, $J = 7.34$ Hz, 2H), 8.28 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 48.5 (C-6′), 57.0 (C-5′), 92.3 (C-2′), 119.2, 119.7, 122.0, 122.7, 129.0, 127.3, 128.0, 128.5–129.8 (8 C–Ar), 132.0, 132.3, 133.2, 140.2, 148.7, 151.2, 171.4 (C-4′); UV/Vis (EtOH) λ_{max}/nm: 255 before irradiation and 260, 370 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 260 before irradiation and 265, 375 nm after irradiation.

*2-[3-(4-Methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl]-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0] hex-3-ene (**9c**)*

Yield: 89%; m.p. 173–174 °C; as a beige solid; IR (KBr, cm^{-1}): 3062, 1597, 1576, 1548, 1511, 1500, 1449, 1437, 1341, 1298, 1252, 1072, 974, 860, 771, 705, 695; (closed-form, 47%): ^{1}H NMR