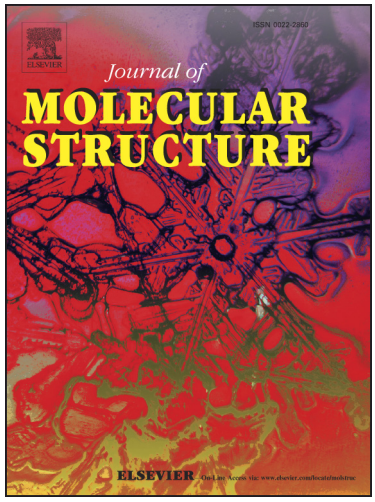

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Synthesis of new pyrazolyl-1,3-diazabicyclo[3.1.0]hexe-3-ene derivatives

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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.

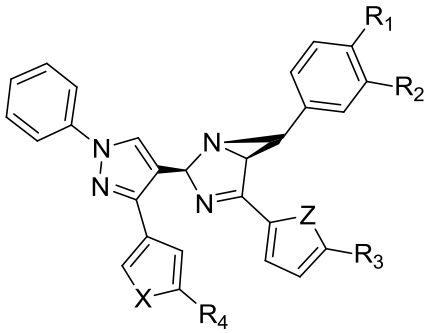
Keywords: Bicyclic aziridine, 1,3-Diazabicyclo[3.1.0]hex-3-ene, Pyrazole carbaldehyde, Photochromic, Vielsmeier-Haack reaction

1. 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].

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.



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.**

2. Experimental

2.1. General

Melting points were measured on a Buchi 510 melting point apparatus and are uncorrected. ^1H 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 as mobile phase. The spots were exposed by UV light.

*2.2. 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-carbaldehydes **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.

2.2.1. 2-(1,3-Diphenyl-1*H*-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, 12H), 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 (500 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, 12H), 7.55-7.57 (m, 2H), 7.60-7.66 (m, 2H), 7.79-7.81(m, 2H), 7.95 (s, 1H, H-pyrazole'), 7.80 (t, J = 6.4 Hz, 2H), 7.99 (s, 1H), 8.02-8.05 (m, 2H), 8.11 (d, J = 8 Hz, 2H), 8.25 (d, J = 8.6 Hz, 2H); ^{13}C NMR (500 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.

2.2.2. 2-(1,3-Diphenyl-1*H*-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 = 1H, 1H), 7.40-7.62 (m, 10H), 7.79-7.83 (m, 2H), 7.97 (s, 1H), 8.02-8.13 (m, 5H), 8.19 (d, J = 7.3 Hz, 2H); ^{13}C NMR (500 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, 10H), 7.79-7.83 (m, 2H), 7.97 (s, 1H), 8.02-8.13 (m, 4H), 8.19 (d, J = 7.34 Hz, 2H), 8.28 (s, 1H); ^{13}C NMR (500 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.

2.2.3. 2-[3-(4-Methoxyphenyl)-1-phenyl-1*H*-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 (500 MHz, $CDCl_3$): δ 2.72 (s, 1H, H-6), 3.74 (dd, J = 1.3,1.8 Hz, 1H, H-5), 3.90 (s, 3H, OCH_3), 6.82 (s, 1H, H-2), 7.03 (d, J = 8.8 Hz, 2H), 7.37 (d, J = 7.2 Hz, 2H), 7.45-7.49 (m, 2H), 7.54-7.62 (m, 4H), 7.77-7.79 (m, 2H), 7.92 (s, 1H, H-pyrazole), 8.01-8.04 (m, 2H), 8.11-8.13 (m, 4H). ^{13}C NMR (500 MHz, $CDCl_3$) δ 48.5 (C-6), 58.3 (C-5), 55.7 (OCH_3), 90.4 (C-2), 114.3, 119.1, 119.6, 123.9, 126.7, 128.9-130.3 (8 CAr), 132.3, 160.1, 171.2 (C-4); after

irradiation with UV light converted to green (open-form, 53%): 2.86 (1H, H-6'), 3.82 (t, *J* = 2.4 Hz, 1H, H-5'), 3.86 (s, 3H, OCH_3'), 6.37 (d, *J* = 2.8 Hz, 1H, H-2'), 6.98 (d, *J* = 8.7 Hz, 2H), 7.30 (m, 2H), 7.45-7.49 (m, 2H) 7.54-7.62 (m, 4H), 7.77-7.79 (m, 2H), 7.96 (s, 1H, H-pyrazole), 8.01-8.04 (m, 4H), 8.26 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (500 MHz, $CDCl_3$): *δ* 42.3 (C-6'), 54.9 (OCH_3), 57.0 (C-5'), 90.4 (C-2'), 114.3, 118.6, 119.6, 124.1, 126.2, 128.9-130.3 (8 C-Ar), 132.4, 160.1, 171.2 (C-4'); UV/Vis (EtOH) λ_{max}/nm: 280 before irradiation and 275, 415 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 275 before irradiation and 275, 420 nm after irradiation.

2.2.4. 2-[3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl]-6-(4-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**9d**):

Yield: 92%, M.p: 177-178 °C; as a lemone solid; IR (KBr, cm^{-1}): 3089, 2858, 1598, 1526, 1447, 1350, 820, 779, 697; (closed-form, 74%): ^{1}H NMR (400 MHz, $CDCl_3$,): *δ* 2.68 (s, 1H, H-6), 3.73 (t, *J* = 1.6 Hz, 1H, H-5), 6.80 (s, 1H, H-2), 7.31-7.62 (m, 10H), 7.76-7.79 (m, 2H), 7.98 (s, 1H, H-pyrazole), 7.99-8.03 (m, 2H), 8.13 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): *δ* 41.8 (C-6), 57.9 (C-5), 89.8 (C-2), 118.5, 118.8, 123.6, 126.7, 127.2, 127.3, 128.6, (C-h), 129.0, 129.4, 129.5, 129.9, 131.3, 132.1, 134.2, 139.7, 144.9, 147.2, 149.6, 171.1 (C-4); after irradiation with UV light converted to green (open-form, 26%): ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.86 (d, *J* = 2.0 Hz, 1H, H-6'), 3.82 (t, *J* = 2.4 Hz, 1H, H-5'), 6.34 (d, *J* = 3.2 Hz, 1H, H-2'), 7.31-7.62 (m, 10H), 7.76-7.79 (m, 2H), 7.93 (s, 1H, H-pyrazole), 7.99-8.03 (m, 2H), 8.06 (d, *J* = 8.8 Hz, 2H), 8.25 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): *δ* 48.1 (C-6'), 56.9 (C-5'), 91.0 (C-2'), 118.8, 119.3, 123.9, 126.7, 127.0, 127.7, 128.5, (C-h'), 128.7, 129.4, 129.5, 129.9, 131.3, 131.8, 134.2), 139.7, 145.0, 147.6, 149.6, 170.0 (C-4'); UV/Vis (EtOH) λ_{max}/nm: 280 before irradiation and 275, 410 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 280 before irradiation and 275, 420 nm after irradiation.

2.2.5. 2-[3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrazol-4-yl]-6-(3-nitrophenyl)-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**9e**):

Yield: 89%, M.p: 187-188 °C; as a white; IR (KBr, cm^{-1}): 3089, 1598, 1526, 1447, 1350, 1217, 1179, 837, 779, 678; (closed-form, 72%): ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.69 (s, 1H, H-6), 3.74 (s, 1H, H-5), 6.81 (s, 1H, H-2), 7.29-7.34 (m, 1H), 7.41-7.63 (m, 8H), 7.76-7.80 (m, 2H), 7.96 (s, 1H, H-pyrazole), 8.00-8.02 (m, 2H), 8.06-8.14 (m, 5H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 41.6 (C-6), 57.7 (C-5), 89.8 (C-2), 118.6, 118.9, 121.6, 122.4, 126.6, 127.8, 128.5-128.6, 128.9, 129.5, 129.6, 130.0, 131.4, 132.0, 132.6, 134.2, 139.9, 148.2, 149.8, 171.1 (C-4); after irradiation with UV light converted to pink (open-form, 28%): ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 2.87 (d, *J* = 1.6 Hz, 1H, H-6'), 3.85 (s, 1H, H-5'), 6.35 (d, *J* = 2.8 Hz, 1H, H-2'), 7.29-7.34 (m, 1H), 7.41-7.63 (m, 8H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.76-7.80 (m, 2H), 8.00-8.02 (m, 3H), 8.06-8.14 (m, 2H), 8.20 (d, *J* = 8.0 Hz, 1H), 8.26 (s, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): *δ* 48.0 (C-6'), 56.5 (C-5'), 91.0 (C-2'), 118.9, 119.3, 121.4, 122.8, 126.6, 127.1, 128.5-128.6, 128.9, 129.3, 129.6, 130.0, 131.3, 132.0, 132.5, 134.1, 139.9, 148.3, 149.8, 169.9 (C-4'); UV/Vis (EtOH) λ_{max}/nm: 260 before irradiation and 269, 370 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 255 before irradiation and 260, 375 nm after irradiation.

2.2.6. 4-(4-Methoxyphenyl)-2-[3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl]-6-(4-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (**9f**):

Yield: 88%; m.p. 195-196 °C; as a pale pinkish solid; IR (KBr, cm^{-1}): 3098, 2834, 1600, 1550, 1448, 1342, 1172, 861, 771, 680; (closed-form, 67%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.69 (s, 1H, H-6), 3.69 (s, 1H, H-5), 3.89 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3,), 6.77 (s, 1H, H-2), 6.96-7.05 (m, 4H), 7.28 (m, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.44-7.47 (m, 2H), 7.76 (d, J = 7.6 Hz, 2H), 7.92 (s, 1H, H-pyrazole), 7.96 (d, J = 8.4 Hz, 2H), 8.09-8.12 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 41.9 (C-6), 55.3 (OCH_3), 55.5 (OCH_3), 57.8 (C-5), 89.7 (C-2), 113.8, 114.3, 118.7, 119.2, 123.5, 124.1, 125.5, 126.3, 127.3, 127.4, 129.4, 129.5, 130.3, 139.1, 145.2, 147.1, 150.7, 159.7, 162.7, 170.2 (C-4); after irradiation with UV light converted to red (open-form, 33%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.83 (s, 1H, H-6′), 3.77 (s, 1H, H-5′), 3.85 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3′), 6.32 (s, 1H, H-2′), 6.96-7.05 (m, 4H), 7.28 (m, 1H), 7.44-7.47 (m, 2H), 7.56 (d, J = 8.4 Hz, 2H), 7.76 (d, J = 7.6 Hz, 2H), 7.93 (s, 1H, H-pyrazole), 7.96 (d, J = 8.4 Hz 2H), 8.02 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 8.4 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 48.2 (C-6′), 55.3 (OCH_3'), 55.5 (C-OCH_3'), 56.8 (C-5′), 90.9 (C-2′), 113.9, 114.3, 118.7, 118.4, 122.1, 123.8, 125.9, 126.4, 126.7, 127.5, 129.3, 129.9, 130.4, 140.1, 145.2, 147.5, 150.9, 159.6, 162.7, 169.1 (C-4); UV/Vis (EtOH) λ_{max}/nm: 290 before irradiation and 290, 425 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 295 before irradiation and 295, 435 nm after irradiation.

2.2.7. 6-(4-Nitrophenyl)-2-[3-(4-nitrophenyl)-1-phenyl-1*H*-pyrazol-4-yl]-4-phenyl-1,3-diazabicyclo[3.1.0]hex-3-ene (**9g**):

Yield: 88%; m.p. 186-188 °C; as a lemon color solid; IR (KBr, cm^{-1}): 3057, 1597, 1511, 1449, 1342, 1246, 770, 682; (closed-form, 78%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.69 (s, 1H, H-6), 3.79 (s, 1H, H-5), 6.83 (s, 1H, H-2), 7.34-7.65 (m, 8H), 7.78-7.81 (d, J = 7.6 Hz, 2H), 7.97-8.07 (m, 3H), 8.13 (d, J = 8.8 Hz, 2H), 8.26-8.35 (m, 2H), 8.46-8.50 (d, J = 8.8 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 41.9 (C-6), 58.0 (C-5), 89.6 (C-2), 119.0, 119.3, 123.7, 123.8, 127.1, 127.2, 128.2, 128.5, 129, 129.5, 131.2, 132.2, 139.2, 139.5, 144.6, 147.4, 148.1, 171.5 (C-4); after irradiation with UV light converted to green (open-form, 22%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.90 (d, J = 1.6 Hz, 1H, H-6′), 3.86 (t, J = 2.4 Hz, 1H, H-5′), 6.38 (d, J = 2.8 Hz, 1H, H-2′), 7.29 (m, 2H), 7.34-7.64 (m, 6H), 7.77-7.81 (d, J = 7.6 Hz, 2H), 7.97-8.06 (m, 5H), 8.26-8.35 (m, 4H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 48.2 (C-6′), 56.0 (C-5′), 90.9 (C-2′), 119.0, 123.7, 123.8, 127.1, 127.2, 128.2, 128.6, 129, 129.5, 131.2, 132.2, 139.2, 139.5, 144.6, 147.4, 148.1, 171.5 (C-4); UV/Vis (EtOH) λ_{max}/nm: 260 before irradiation and 265, 405 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 260 before irradiation and 265, 415 nm after irradiation.

2.2.8. 6-(4-Nitrophenyl)-4-phenyl-2-(1-phenyl-3-thiophen-2-yl-1*H*-pyrazol-4-yl)-1,3-diazabicyclo[3.1.0]hex-3-ene (**9h**):

Yield: 85%; m.p. 168-169 °C; as a beige solid; IR (KBr, cm^{-1}): 3073, 1597, 1566, 1509, 1447, 1339, 1218, 831, 763, 688; (closed-form, 57%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.70 (s, 1H, H-6), 3.76 (s, 1H, H-5), 6.83 (s, 1H, H-2), 7.20 (m, 1H), 7.29-7.62 (m, 9H), 7.74-7.79 (m, 2H), 7.89 (s, 1H), 8.02-8.05 (m, 2H), 8.02-8.05 (s, 1H), 8.11-8.15 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 42.0 (C-6), 57.9 (C-5), 89.6 (C-2), 117.8, 118.8, 121.7, 123.6, 125.4, 126.5, 126.7, 127.3, 127.5, 127.7, 128.6, 128.9, 129.4, 131.4, 132.8, 135.1, 139.5, 145.5, 147.5, 171.3 (C-4); after irradiation with UV light converted to blue (open-form, 43%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91 (d, J = 1.6 Hz, 1H, H-6'), 3.81 (t, J = 2.4 Hz, 1H, H-5'), 6.45 (d, J = 2.4 Hz, 1H, H-2'), 7.10 (m, 1H), 7.29-7.62 (m, 9H), 7.74-7.79 (m, 3H), 7.94 (s, 1H), 8.11-8.15 (m, 2H), 8.25 (d, J = 8.8 Hz, 2H); ^{13}C NMR (400 MHz,

$CDCl_3$): δ 48.0 (C-6'), 56.9 (C-5'), 90.9 (C-2'), 117.6, 119.2, 121.7, 123.8, 125.4, 126.4, 126.7, 127.3, 127.5, 127.6, 128.7, 128.9, 129.4, 131.3, 132.8, 135.3, 139.8, 145.0, 147.2, 170.3 (C-4'); UV/Vis (EtOH) λ_{max}/nm: 260, 290 before irradiation and 285, 415 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 260, 290 before irradiation and 290, 420 nm after irradiation.

2.2.9. 6-(3-Nitrophenyl)-4-phenyl-2-(1-phenyl-3-thiophen-2-yl-1*H*-pyrazol-4-yl)-1,3-diazabicyclo[3.1.0]hex-3-ene (**9i**):

Yield: 87%; m.p. 204-205 °C; as a pinkish solid; IR (KBr, cm^{-1}): 3095, 2861, 1598, 1561, 1504, 1378, 1234, 822, 779, 695; closed-form: 88%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.71 (d, *J* = 0.8 Hz, 1H, H-6), 3.77 (dd, *J* = 1.2, 1.6 Hz, 1H, H-5), 6.84 (s, 1H, H-2), 7.20-7.22 (m, 1H), 7.29 (t, *J* = 76 Hz, 1H), 7.37 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.42-7.48 (m, 3H), 7.54-7.62 (m, 4H), 7.75 (dd, *J* = 0.8, 8.4 Hz, 2H), 7.90 (s, 1H), 8.02-8.04 (m, 2H), 8.07-8.10 (m, 1H), 8.14-8.17 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 41.8 (C-6), 57.6 (C-5), 89.6 (C-2), 117.8, 121.8, 122.4, 125.7, 126.5, 126.9, 127.6, 127.8, 128.6, 128.9, 129.3, 129.4, 131.4, 132.0, 132.8, 135.0, 139.8, 139.9, 145.7, 148.3, 171.4 (C-4); after irradiation with UV light converted to pinkish (open-form, 22%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.92 (d, *J* = 2.0 Hz, 1H, H-6'), 3.83 (m, 1H, H-5'), 6.47 (d, *J* = 2.8 Hz, 1H, H-2'), 7.10-7.12 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.42-7.48 (m, 4H), 7.54-7.62 (m, 4H), 7.75 (dd, *J* = 0.8, 8.4 Hz, 2H), 7.79-7.81 (m, 1H),7.97 (s, 1H), 8.02-8.04 (m, 2H), 8.19-8.23 (m, 1H), 8.30 (m, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 48.0 (C-6'), 56.9 (C-5'), 91.1 (C-2'), 118.8, 119.3, 121.7, 122.4, 125.7, 126.5, 126.9, 127.6, 127.8, 128.6, 128.9, 129.3, 129.4, 131.4, 132.0, 132.8, 135.0, 139.8, 139.9, 145.7, 148.3, 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: 290 before irradiation and 290, 375 nm after irradiation.

2.2.10. 2-(3-(4-methoxyphenyl)-1-phenyl-1*H*-pyrazol-4-yl)-6-(4-nitrophenyl)-4-(thiophen-2-yl)-3,5-diazabicyclo [3.1.0] hex-2-ene (**9j**):

Yield: 79%; m.p. 167-168 °C; as a white solid; IR (KBr, cm^{-1}): 3082, 1598, 1514, 1449, 1345, 1247, 1178, 821, 784, 680; closed-form: 78%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.72 (s, 1H, H-6), 3.69 (s, 1H, H-5), 3.89 (s, 3H, OCH_3), 6.77 (s, 2H, H-2), 7.00 (d, *J* = 8.8 Hz, 2H), 7.19-7.21 (m, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.53-7.56 (m, 1H), 7.64 (m, 3H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.91 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 41.8 (C-6), 55.3 (OCH_3), 57.9 (C-5), 89.6 (C-2), 113.9, 118.8, 119.2, 123.5, 125.4, 126.4, 127.3, 127.4, 128.1, 129.3, 129.4, 130.0, 131.4, 135.7, 139.8, 144.8, 147.2, 150.6, 159.7, 165.0 (C-4); after irradiation with UV light converted to blue (open-form, 22%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.87 (d, *J* = 1.2 Hz, 1H, H-6′), 3.75 (s, 1H, H-5′), 3.85 (s, 3H, OCH_3), 6.29 (d, *J* = 1.4 Hz, 1H, H-2′), 6.95 (d, *J* = 8.8 Hz, 2H), 7.19-7.21 (m, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.53-7.56 (m, 1H), 7.64 (m, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.91 (s, 1H), 8.06 (d, *J* = 8.8 Hz, 2H), 8.25 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 48.1 (C-6′), 55.3 (OCH_3), 56.9 (C-5′), 91.0 (C-2′), 114.0,117.9, 118.8, 123.8, 125.4, 126.4, 127.1, 127.5, 128.1, 129.3, 129.4, 130.0, 131.2, 135.7, 139.8, 144.8, 147.2, 150.6, 159.7, 165.0 (C-4′); UV/Vis (EtOH) λ_{max}/nm: 290 before irradiation and 295, 430 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 295 before irradiation and 295, 430 nm after irradiation.

2.2.11. 4-(4-Methoxyphenyl)-6-(4-nitrophenyl)-2-(1-phenyl-3-thiophen-2-yl-1*H*-pyrazol-4-yl)-1,3-diazabicyclo-[3.1.0]hex-3-ene (**9k**):

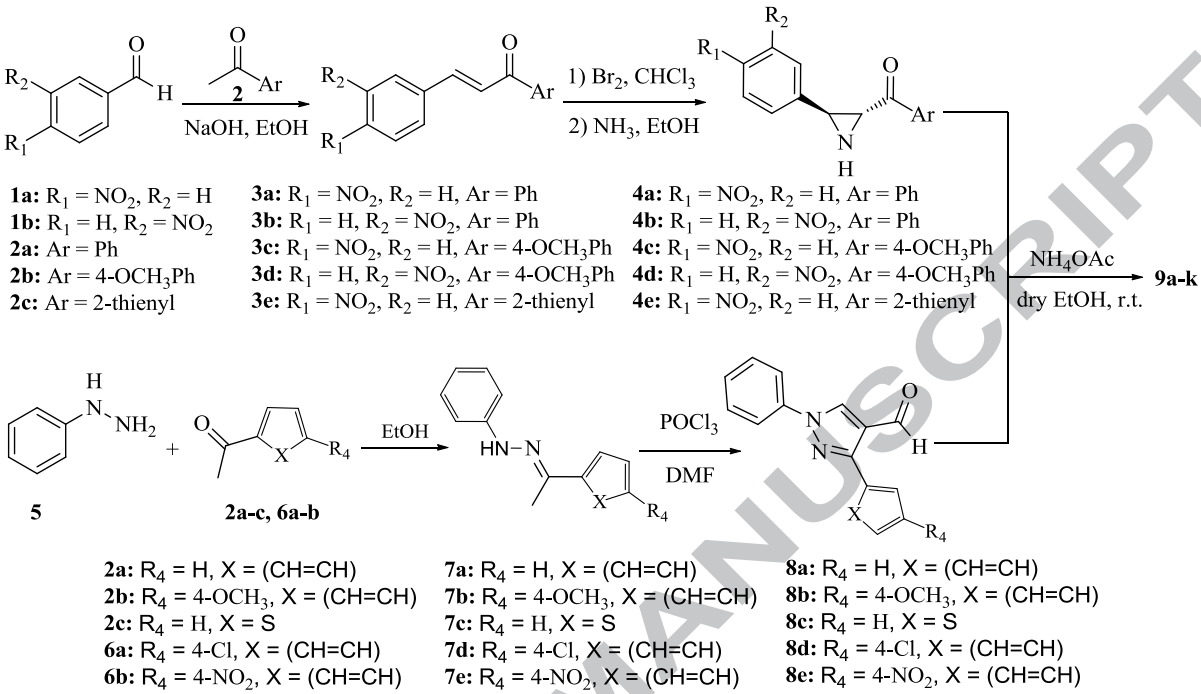
Yield: 79%; m.p. 167-168 °C; as a white solid; IR (KBr, cm^{-1}): 3105, 2934, 2841, 1599, 1508, 1464, 1341, 1216, 819, 795, 689; closed-form: 62%, ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.68 (s, 1H, H-6), 3.72 (s, 1H, H-5), 3.93 (s, 3H, OCH_3), 6.79 (s, 1H, H-2), 7.03-7.06 (m, 2H), 7.18-7.20 (m, 1H), 7.31-7.49 (m, 6H), 7.74-7.79 (m, 2H), 7.90 (s, 1H), 7.96-7.99 (m, 4H), 8.11-8.15 (m, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 42.0 (C-6), 55.5 (OCH_3), 57.8 (C-5), 89.4 (C-2), 114.3, 118.9, 119.2, 123.6, 124.2, 125.7, 126.5, 126.6, 126.8, 127.5, 127.7, 129.4, 130.3, 135.1, 139.5, 145.4, 147.2, 162.6, 170.5 (C-4); after irradiation with UV light converted to green-blue (open-form, 38%): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.88 (d, J = 1.6 Hz, 1H, H-6'), 3.77 (s, 1H, H-5'), 3.92 (s, 3H, OCH_3'), 6.40 (d, J = 1.6 Hz, 1H, H-2'), 7.03-7.06 (m, 2H), 7.09-7.11 (m, 1H), 7.31-7.49 (m, 4H), 7.58 (d, J = 8.8 Hz, 2H), 7.74-7.79 (m, 3H), 7.93 (s, 1H), 8.11-8.15 (m, 2H), 8.25 (d, J = 8.0 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 47.9 (C-6'), 55.5 (OCH_3'), 56.8 (C-5'), 90.7 (C-2'), 114.3, 118.0, 118.9, 123.8, 124.1, 125.7, 126.6, 126.7, 126.8, 127.3, 127.6, 129.4, 130.4, 135.4, 139.8, 145.2, 147.5, 162.6, 169.5 (C-4'); UV/Vis (EtOH) λ_{max}/nm: 290 before irradiation and 290, 425 nm after irradiation; UV/Vis (DCM) λ_{max}/nm: 290 before irradiation and 290, 435 nm after irradiation.

3. Results and Discussion

The structures of photochromic pyrazolyl bicyclic aziridine compounds (**9a-k**) are shown in Fig. 1. Synthetic route to the target compounds as well as required intermediates **4a-e** and **8a-e** is outlined in Scheme 1. 1-Phenyl-3-arylpyrazole-4-carbaldehydes (**8a-e**) were readily prepared according to the procedures previously described in the literature [60, 61]. Firstly, the reaction of arylmethyl ketones (**2a-c** and **6a-b**) with phenyl hydrazine (**5**) under solvent-free conditions led to the formation of the corresponding phenylhydrazone derivatives (**7a-e**). In the next step, pyrazole aldehydes (**8a-e**) were obtained by the reaction of phenylhydrazone derivatives with dimethylformamide (DMF) and phosphorus oxychloride ($POCl_3$) under Vilsmeier-Haack reaction conditions.

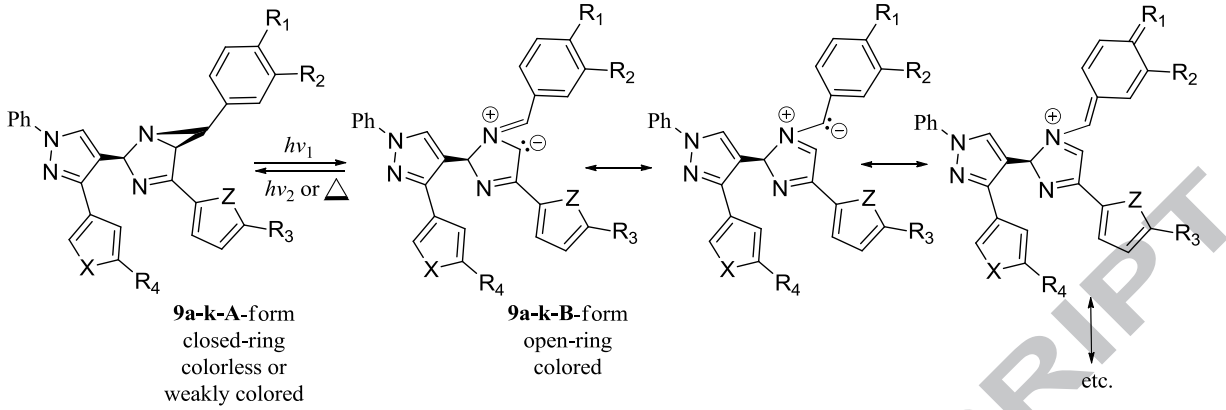
Ketoaziridines (**4a-e**) were synthesized according to the methods described in earlier works [24, 25]. α,β-Unsaturated ketones (chalcones) (**3a-e**) have been prepared by the Claisen-Schmidt condensation, which subjected direct bromination with a solution of bromine in chloroform to afford the corresponding dibromochalcones. Cyclization of dibromochalcones *via* treatment of them with ammonia solution leads to corresponding ketoaziridines (**4a-e**). Target compounds (**9a-k**) were prepared from equimolar quantities of premade ketoaziridines (**4a-e**) and pre-synthesized pyrazole aldehydes (**8a-e**) in the presence of 10 equivalents ammonium acetate, in a one-pot, three-component C—C bond formation and cyclization under anhydrous conditions. The structures of newly prepared compounds (**9a-k**) were confirmed by spectroscopic methods. The synthesized compounds, showed in the IR spectrum strong band at around of 1600 cm^{-1} due to the presence of a C═N group. Moreover, the presence of —NO_2 functional group can give rise to the appearance two strong bands at around of 1525 and 1325 cm^{-1}. In the IR spectrum, absorption bands belonging to the carbonyl and aziridine NH groups in the ketoaziridines (**4a-e**), as well as aldehyde functional group in the pyrazole aldehydes (**8a-e**) disappeared. The peaks arising from aziridine NH and aldehyde functional group are absent from the ^{1}H NMR spectra of target compounds, which supports the formation of products. Also, no peak was observed in the

aldehyde and ketone regions in the ^{13}C NMR spectra of each of the desired compounds **9a-k**, confirming the absence of a carbonyl group in these products.



Scheme 1. Synthetic rout for the preparation of photochromic compounds (**9a-k**) and intermediates (**4a-e** and **8a-e**).

All of these bicyclic aziridine derivatives showed good photochromic both in the solution and crystalline phases. The proposed photochromic reaction of target molecules (**9a-k**) is shown in Scheme 2. In the ^{1}H NMR and ^{13}C NMR (in $CDCl_3$) spectra of synthesized compounds (**9a-k**), two groups of absorptions corresponding to closed-ring and open-ring photoisomers appeared. The ^{1}H NMR spectra of pyrazolyl bicyclic aziridine derivatives (**9a-k**), showed characteristic sets of signals attributed to the protons of aziridine ring (*i.e.*, H-5 and H-6) and proton of C-2 position. The ratio of closed-form and open-form photoisomers were measured by area integration of the some characteristic peaks at around δ 2.68-2.87, 3.74-3.92, and 6.40-6.86 ppm in ^{1}H NMR spectra corresponding to the two photoisomers relative to each other. For instance, according to the ^{1}H NMR of compound **9h** that is shown in Fig. 2, the signals related to the two photoisomers are characterized. In the ^{1}H NMR of compound **9h**, H-2 appeared at δ = 6.84 ppm as a singlet, while proton H-2' were observed at δ = 6.45 ppm. Also, the ^{1}H NMR spectrum of compound **9h** showed a singlet peak at δ = 2.70 ppm because of H-5, a peak at δ = 2.91 ppm due to H-5', a peak at δ = 3.76 ppm because of H-6, and a peak at δ = 3.81 for the H-6' proton. Other signals have appeared in the desired areas.



Scheme 2. Proposed photochromic color change in pyrazolyl-bicyclic aziridines (**9a-k**).

The photochromic reversible color change of pyrazolyl-bicyclic aziridinyl targeted compounds (**9a-k**) is ascribed to photo-induced ring-opening reaction involve the C-N bond cleavage and C-N bond reformation of aziridine moieties (Scheme 2). This photochromic process was confirmed by changes in the UV-Vis spectra. Absorption spectral changes of these photochromic compounds in EtOH and dichloromethane (DCM) solutions were changed under UV light at ambient temperature. For example, the ring-closed isomer of bicyclic aziridine **9a-A**-form exhibits slight conjugation and consequently lacks of absorption in the visible region of the spectrum. However, it can absorb a photon in the ultraviolet region of the spectrum and its aziridine moiety can undergo an electrocyclic ring-opening reaction to yield the open isomer **9a-B**-form.

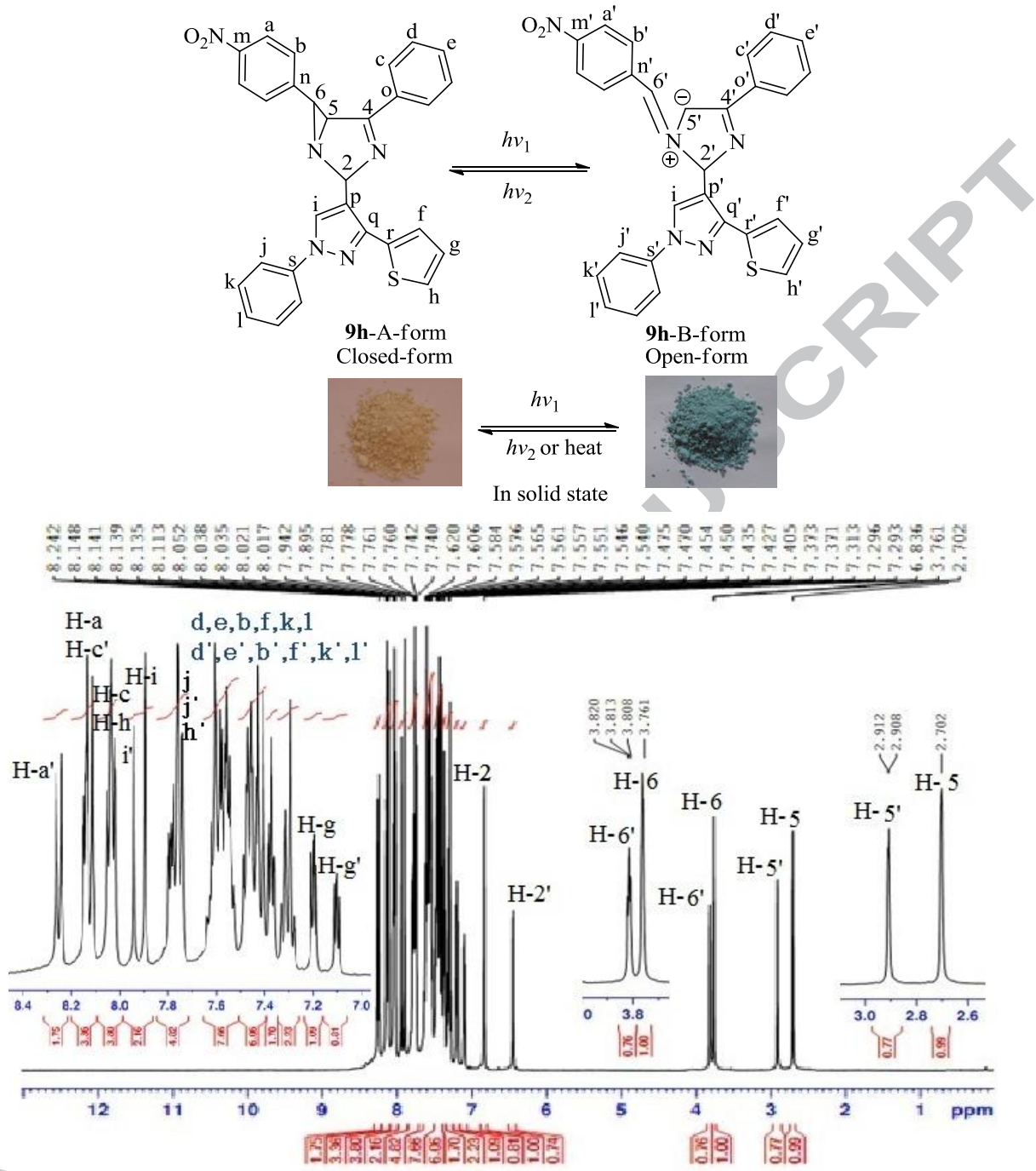


Fig. 2. Photochromic color change in solid state (up) and ^{1}H NMR of compound **9h** (bottom).

The installation of an azomethine ylide moiety in the ring-open isomer leads to a longer π-system, which has an electronic transition corresponding to photons in the visible region of the spectrum; this isomer, upon absorption of visible light, undergoes a cyclization reaction to generate the ring-closed isomer. Exposure of the solutions of **9h-A**-form to UV light (centered on 365 nm) induces a color change in the solution from colorless (**9h-A**-form) to yellow (**9h-B**-form). This photochromic color change occurs in EtOH and DCM solutions, whereas color change in solid state occurs from pale beige crystals (**9h-A**-form) to blue crystals (**9h-B**-form). Upon irradiation with UV light, compound **9a-A**-form underwent a photochromic reaction; this goes along with noticeable changes in the absorption spectra as shown in Fig. 3.

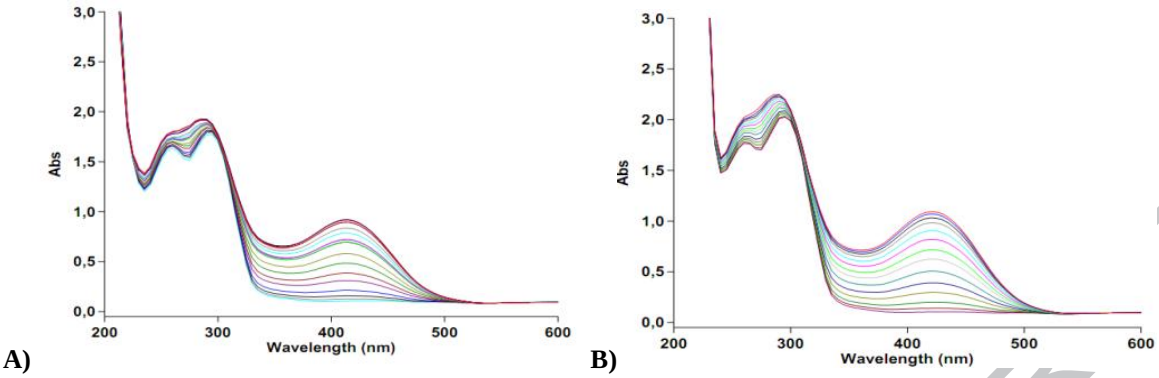


Fig. 3. Overlay UV/Vis spectral changes of 9h under 365 nm irradiation at ambient temperature (A) in EtOH solution (3.0×10^{-4} mol/L) and (B) in DCM solution (3.0×10^{-4} mol/L), time irradiation from bottom to up: 0, 3, 6, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60 sec.

The change in the absorption spectra of **9h** in EtOH induced by irradiation with UV light is shown in Fig. 3A. Before irradiation with UV light, there is no band in the visible region. After UV irradiation of the solution, absorption bands appeared in the visible region. Before irradiation, closed isomer of **9h** showed a sharp absorption peaks at 260 and 290 nm in EtOH. Upon irradiation with 365 nm light, new visible absorption bands focused at 285 and 415 nm were appeared. The appearance of these new bands is ascribable to the formation of the open-ring isomer **9h-B**-form. This could be seen with the naked eye, as the colorless solution of **9h** turned yellow. As expected, with increased irradiation time, intensity of the absorption band in the visible region is gradually increased, which indicates that the ring-opening reaction occurs. The spectral changes showed that **9h** display photochromic behavior, similar to known polyaryl-1,3-diazabicyclo[3.1.0]hex-3-enes [12-37]. In DCM solution, **9h** also exhibited similar photochromic color change to that in EtOH. The changes in the absorption spectra of **9h** are shown in Fig. 3B. Upon irradiation with 365 nm UV light, the colorless solution of **9h** turned yellow, of which the absorption maximum was observed at 420 nm in consequence of the formation of the open-ring isomer **9h-B**-form. Also, an isosbestic point around 300 nm in Fig. 3A and 305 nm in Fig. 3B, showed the presence of two species **9h-A**-form and **9h-B**-form. Color change in the solid and solution states was observed by eye-naked, when compounds are exposed to light (UV light from mercury, xenon lamp, fluorescent lamp or sunlight) at ambient temperature. By increasing the duration of irradiation or exposure to sunlight the intensity of color form enhances, owing to the increase of population of open-form in the crystal states. In this condition the weakly colored **9a-k-A**-forms changes to colored solids **9a-k-B**-forms.

4. Conclusions

In conclusion, the eleven representatives of 1,3-diazabicyclo[3.1.0]hex-3-enes containing pyrazole moieties at C-2 position and thiophene fragment at C-4 or pyrazole moieties have been obtained. Their structures of targeted intelligent materials have been characterized by NMR, absorption spectral data, and IR measurements. The photochromic behaviors all newly synthesized compounds have been studied by UV-Vis spectral changes. It was found that all of the bicyclic synthesized compounds exhibit good photochromic reactivity in the both solution and solid phases upon irradiation with UV light.

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GRAPHICAL ABSTRACT

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

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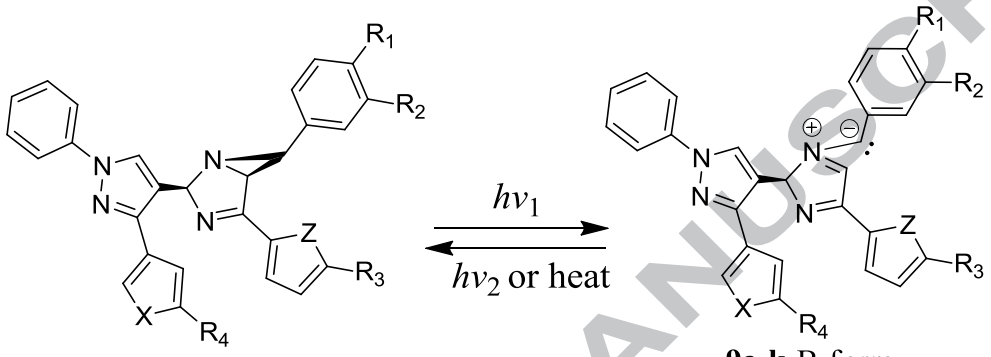

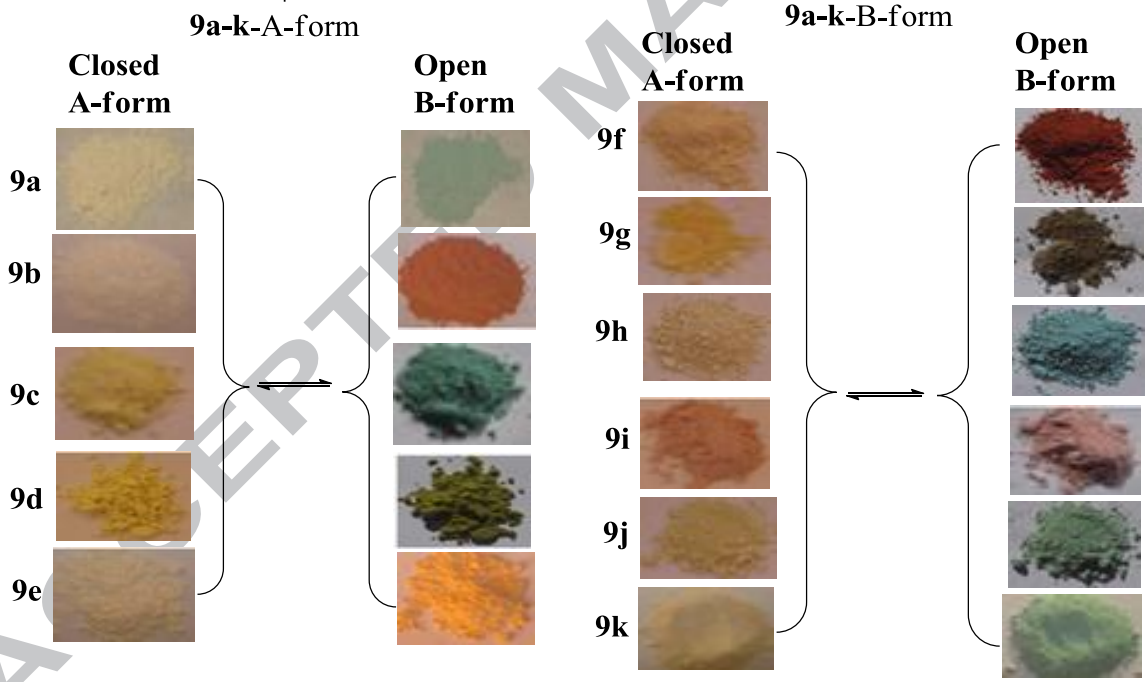

Highlights

- 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 solid and solution phases.
- 1,3-Diazabicyclo[3.1.0]hex-3-enes containing thiophene fragment have been synthesized.