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A facile route to the new triazene dyes based on substituted pyrazolidin-3,5-dione derivatives

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ABSTRACT

Several substituted triazenes dyes were synthesized by coupling functionalized pyrazolidin-3,5-dione derivatives, to various heteroarene azides in excellent yields (98%). Electron delocalization between the two coupled components of these triazene dyes was studied using UV–vis spectra and NMR spectroscopy. Their thermolysis was investigated and by using an isotopically labeled triazene, the mechanism decomposition reaction was also identified. The protolysis of these triazenes was evaluated and showed that they are highly stable and even in strongly acidic medium.

1. Introduction

Triazenes are rather 'old' compounds from the organic chemist's viewpoint. It was as early as 1862 that Griess described a suitable way for the synthesis of 1,3-diphenyltriazene as a unique polyazo compound containing three consecutive nitrogen atoms in an acyclic form [1–4]. They are known as a versatile tool in organic synthesis [3]. Although they are studied for their anorectic activity [5] and potency against specific tumor cell lines [6,7], applied as protecting groups in natural product synthesis [8,9], or used to form heterocycles [10–12], most reports describe their applications as useful linkers in solid-phase organic synthesis [13–15]. We distinguish two most suitable routes for the synthesis of triazenes (1) the coupling of aryl diazonium salts to amines [2,16,17] and (2) the addition of organometallic reagents (RMgX, RLi, etc.) to alkyl azides [18,19]. However, the reagents used in these synthetic strategies are extremely reactive, and generally flammable, which necessitates the use of special equipment and safety measures. As a result, the scope of compatible substrates and the range of associated applications for preparing triazenes are restrictive. These limitations require the development of new methods for accessing this important class of donor acceptor systems. Recently, a new, practical method for preparing triazenes was reported [20,21], the authors specified that addition of a *N*-heterocyclic carbene [22–25] (NHC) to an organic azide afford 1,3-di-substituted triazene in excellent to moderate yield [26]. Following this study, the NHC/azide coupling reaction is considered a similar to the copper-catalyzed [3 + 2] alkyne–azide "click" coupling [27–30]. In addition to the practical advantages discussed above, the NHC/azide coupling reaction presents two features for this purpose: chemical unsaturation is conserved as reactants are converted to products and the triazene bridge formed formally conjugates the two organic components to each other.

On the other hand, nitrogen heterocycles are of special interest because they constitute an important class of natural and non-natural products, many of them exhibit useful biological activities and unique electrical and optical properties [31–35], pyrazolidin-3,5-dione derivatives are one of these nitrogen heterocycles and they are in general well-known five-membered nitrogen-containing heterocyclic compounds. Recently, we developed a new class of azo- and H-chromophore dyes based on pyrazolidin-3,5-dione

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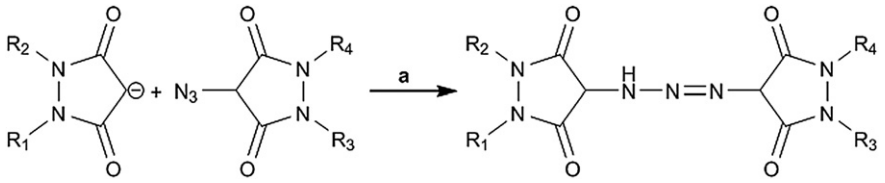


Scheme 1. Triazene system synthesis via coupling of pyrazolidin-3,5-dione with its corresponding azide. Reagent and conditions: (a) NaH, THF, RT.

derivatives [36]. The pyrazolidin-3,5-dione was chosen for its electron donor character because of the removal of the hydrogen atom in the alpha carbonyl group position (*C-4*) of pyrazolin-3,5-dione in basic conditions. Due to the possible electron donor character of pyrazolidin-3,5-diones, in this paper we report the synthesis of donor–acceptor triazene systems based on pyrazolidin-3,5-dione and its corresponding azide as building blocks (Scheme 1).

The aims of this work were the synthesis of the new class of "donor–acceptor" triazenes **4a**–**i** based on various the pyrazolidin-3,5-dione **NHCPyr** derivatives and their coupling to organic azides **AzPyr** possessing complementary functional groups. The second objective was to study the electronic properties of the synthesized conjugated π-triazenes dyes.

2. Experimental

2.1. Chemicals and materials

All chemicals were reagent grade (Aldrich Chemical Co.) and were used as purchased without further purification. Thin layer chromatography was carried out on silica gel pre-coated plates (Merck; 60 Å F254) and spots located with (a) UV light (254 and 366 nm), (b) I_2 or (c) a basic solution of permanganate [$KMnO_4$ (3 g), K_2CO_3 (20 g) and NaOH (0.25 g) in water (300 mL)]. Flash column chromatography (FCC) was carried out on Merck silica gel 60 (230–400 mesh) according to Still et al. [37]. ^{1}H and ^{13}C NMR spectra were recorded at 200 MHz with Varian spectrometers in deuterated solvents and are reported in parts per million (ppm) with the solvent resonance used as the internal reference. Mass spectra were recorded with a Thermo Fisher LCQ fleet ion-trap instrument (the spectra exported were also using the ESI + *c* technique). Elemental analysis was carried out with a Perkin–Elmer 240 C Elemental Analyzer. UV/vis spectra were recorded with a Cary-4000 Varian spectrophotometer. Samples for thermogravimetric characterization were located in open platinum crucibles and analyzed using a Rheometric Scientific TG1000 thermobalance operating under a flowing argon atmosphere (28 mL min^{-1}). A heating rate of 10 °C min^{-1} was used and all samples were studied between 30 and 400 °C. Literature methods [15] were used to prepare compounds **1a**–**e** (**1e**, R = Br).

2.2. General procedure A: synthesis of the 4-bromopyrazolidin-3,5-dione derivatives

To a suspension of pyrazolidin-3,5-dione derivatives (1 mmol) in THF (10 mL), NBS (1 mmol) was added and the resulting mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure and the resulting colorless oil was passed through short silica column to give crude mixture including the desired products **2a**–**d** and the starting pyrazolidin-3,5-dione derivatives (the percentages were measured by NMR integral).

2.2.1. 4-Bromo-1-phenylpyrazolidin-3,5-dione (*2a*)

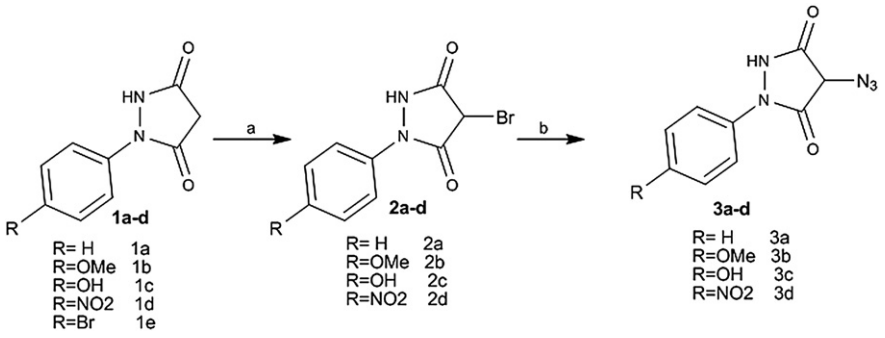
The product **2a** was prepared according to the general procedure *A* using the following quantities: 1-phenylpyrazolidin-3,5-dione **1a** (1.00 g, 5.68 mmol), NBS (0.98 g, 5.68 mmol) in THF (15 mL) to afford **1a** (1.79 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02 (s, N*H*), 7.37–7.35 (m, 4H), 6.89 (m, 1H), 5.32 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.4, 165.8, 134.8, 132.3, 128.9, 128.0, 65.9 ppm. MS (ESI): m/z = 254.06 $[M+1]^+$.

2.2.2. 4-Bromo-1-(4′-methoxyphenyl)pyrazolidin-3,5-dione (*2b*)

The product **2b** was prepared according to the general procedure *A* using the following quantities: 1-phenylpyrazolidin-3,5-dione **1b** (1.00 g, 5.68 mmol), NBS (0.98 g, 5.68 mmol) in THF (15 mL) to afford **2b** (1.79 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.01 (s, N*H*), 7.30 (m, 2H), 6.92 (m, 2H), 5.33 (s, 1H), 3.84 (s, 3H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 170.3, 165.7, 158.8, 127.3, 125.6, 114.5, 65.8, 55.8 ppm. MS (ESI): m/z = 255.03 $[M+1]^+$.

2.2.3. 4-Bromo-1-(4′-hydroxyphenyl)pyrazolidin-3,5-dione (*2c*)

The product **2c** was prepared according to the general procedure *A* using the following quantities: 1-phenylpyrazolidin-3,5-dione **1c** (1.00 g, 5.20 mmol), NBS (0.97 g, 5.20 mmol) in THF (15 mL) to afford **2c** (1.78 g, 95%). ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.02 (s, N*H*),



Scheme 2. Synthesis of pyrazolidin-3,5-dione azide derivatives (**AzPyr**). Reagent and conditions: (a) NBS, THF, RT, 2 h, (b) NaN_3, acetonitrile, 80 °C, 8 h.

7.24 (m, 2H), 6.88 (m, 2H), 5.32 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.4$, 165.8, 154.1, 127.4, 126.0, 116.2, 65.8 ppm. MS (ESI): $m/z = 271.04$ $[M+1]^+$.

*2.2.4. 4-Bromo-1-(4-nitro)phenylpyrazolidin-3,5-dione (**2d**)*

The product **2d** was prepared according to the general procedure *A* using the following quantities: 1-(4-nitro)-phenyl-pyrazolidin-3,5-dione **1d** (0.99 g, 4.52 mmol), NBS (0.45 mL, 4.52 mmol) in THF (15 mL) to afford **2d** (1.55 g, 92%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.16$ (m, 2H), 8.03 (s, N*H*), 7.09 (m, 2H), 5.33 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.3$, 165.9, 140.9, 143.5, 124.1, 122.5, 65.8 ppm. MS (ESI): $m/z = 299.98$ $[M+1]^+$.

2.3. General procedure B: synthesis of the 4-azidopyrazolidin-3,5-dione derivatives

To a suspension of 4-bromo pyrazolidin-3,5-dione derivatives (1 mmol) in acetonitrile (15 mL), NaN_3 (1 mmol) was added and the resulting mixture was stirred at 80 °C for 8 h. The solvent was removed under reduced pressure and the reaction mixture was purified by flash column chromatography (EtOAc/hexane 10/7) to afford the pure products **3a**–**d**.

*2.3.1. 4-Azido-1-phenylpyrazolidin-3,5-dione (**3a**)*

The product **3a** was prepared according to the general procedure *B* using the following quantities: **2a** (1.00 g, 3.95 mmol), NaN_3 (0.28 g, 3.95 mmol) in acetonitrile (15 mL) to afford **3a** (0.84, 99%). $R_f = 0.45$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.02$ (s, N*H*), 7.37–7.34 (AA′XX′ system, 4H), 7.12 (s, 1H, N*H*), 6.89 (m, 1H), 3.22 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.3$, 165.8, 134.7, 132.5, 128.8, 128.1, 83.9 ppm. MS (ESI): $m/z = 218.11$ $[M+1]^+$. $C_9H_7N_5O_2$ (217.06): calcd C, 49.77; H, 3.25; N, 32.25, found, C, 49.81; H, 3.29; N, 32.28.

*2.3.2. 4-Azido-1-(4′-methoxy)phenylpyrazolidin-3,5-dione (**3b**)*

The product **3b** was prepared according to the general procedure *B* using the following quantities: **2b** (1.00 g, 3.92 mmol), NaN_3 (0.27 g, 3.92 mmol) in acetonitrile (15 mL) to afford **3b** (0.83, 99%). $R_f = 0.44$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.01$ (s, N*H*), 7.31–6.91 (AA′XX′ system, 4H), 7.15 (s, 1H, N*H*), 3.83 (s, 3H), 3.24 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.5$, 165.6, 158.8, 127.4, 125.9, 114.7, 83.6, 55.6 ppm. MS (ESI): $m/z = 248.11$ $[M+1]^+$. $C_{10}H_9N_5O_3$ (247.07): calcd C, 48.58; H, 3.67; N, 28.33, found, C, 48.61; H, 3.70; N, 28.38.

*2.3.3. 4-Azido-1-(4′-hydroxyl)phenylpyrazolidin-3,5-dione (**3c**)*

The product **3c** was prepared according to the general procedure *B* using the following quantities: **2c** (1.00 g, 3.70 mmol), NaN_3 (0.25 g, 3.70 mmol) in acetonitrile (15 mL) to afford **3c** (0.79, 99%). $R_f = 0.49$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.01$ (s, N*H*), 7.25–6.88 (AA′XX′ system, 4H), 7.12 (s, 1H, N*H*), 3.24 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.7$, 165.6, 154.6, 127.6, 126.3, 116.4, 84.6 ppm. MS (ESI): $m/z = 234.09$ $[M+1]^+$. $C_9H_7N_5O_3$ (233.05): calcd C, 46.36; H, 3.03; N, 30.03, found, C, 46.39; H, 3.07; N, 30.07.

*2.3.4. 4-Azido-1-(4-nitro) phenylpyrazolidin-3,5-dione (**3d**)*

The product **3d** was prepared according to the general procedure *B* using the following quantities: **2d** (0.99 g, 3.43 mmol), NaN_3 (0.23 mL, 3.43 mmol) in acetonitrile (15 mL) to afford **3d** (0.75 g, 99%). $R_f = 0.51$. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.15$–7.08 (AA′XX′ system, 4H), 8.02 (s, N*H*), 7.12 (s, 1H, N*H*), 3.23 (s, 1H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 170.1$, 165.6, 140.5, 143.9, 124.8, 122.6, 83.6 ppm. MS (ESI): $m/z = 262.05$ $[M+1]^+$. $C_9H_6N_6O_4$ (262.12): calcd C, 41.23; H, 2.31; N, 32.05, found, C, 41.27; H, 2.35; N, 32.09.

2.4. General procedure C: synthesis of pyrazolidin-3,5-dione triazenes

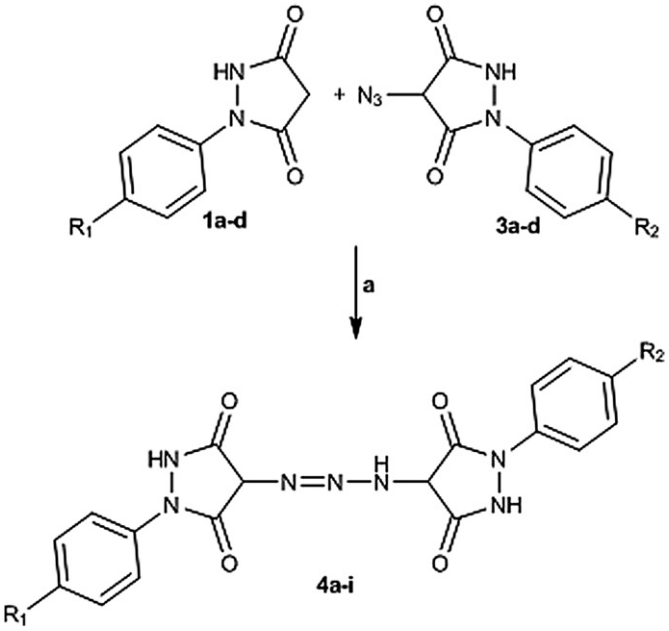
A free pyrazolidin-3,5-dione derivatives (1 equiv) was dissolved in THF (approximate concn = 0.3 M), and treated by NaH (1 mol) for 30 min. Then, azidopyrazolidin-3,5-dione (1 equiv) was added in a single portion and the resulting reaction mixture was stirred for up to 8 h at ambient temperature. Solvent was then removed under reduced pressure to obtain a colorless solid. The product was purified by flash chromatography (alumina, ethyl acetate/hexane 9:4) to afford the desired triazene.

*2.4.1. Bis (1-phenylpyrazolidin-3,5-dione) triazene (**4a**)*

The product **4a** was prepared according to the general procedure *C* using the following quantities: **1a** (1.00 g, 5.68 mmol), **3a** (1.23 g, 5.68 mmol) in THF (15 mL) to afford **4a** (0.75 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.41$ (s, 1H, N*H*), 8.13 (s, 2H, N*H*), 7.37–7.34 (AA′XX′ system, 8H), 6.91 (m, 2H), 4.51 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.1$, 165.6, 140.1, 129.9, 128.5, 124.2, 120.4, 79.7, 76.1 ppm. MS (ESI): $m/z = 394.47$ $[M+1]^+$. $C_{18}H_{15}N_7O_4$ (393.36): calcd C, 54.96; H, 3.84; N, 24.93, found, C, 54.99; H, 3.88; N, 24.97.

*2.4.2. 1-(4-Bromophenyl)-4-(3-(3,5-dioxo-1-phenylpyrazolidin-4-ylidene)triazylidene)pyrazolidin-3,5-dione (**4b**)*

The product **4b** was prepared according to the general procedure *C* using the following quantities: **1e** (1.43 g, 3.95 mmol), **3b** (0.86 g, 3.95 mmol) in THF (15 mL) to afford **4b** (1.85 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.41$ (s, 1H, N*H*), 8.12 (s, 2H, N*H*), 7.52–6.71 (AA′XX′ system, 4H), 7.38–7.35 (AA′XX′ system, 4H), 6.91 (m, 1H), 4.52 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.4$, 165.5, 140.6, 139.8, 132.4, 128.7, 124.5, 122.6, 120.4, 118.3, 79.7, 75.2 ppm. MS (ESI): $m/z = 472.12$ $[M+1]^+$. $C_{18}H_{14}BrN_7O_4$ (471.03): calcd C, 45.78; H, 2.99; N, 20.76, found, C, 45.81; H, 3.07; N, 20.81.



Scheme 3. Synthesis of pyrazolidin-3,5-dione triazene. Reagent and conditions: (a) NaH, THF, RT.

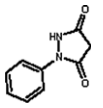
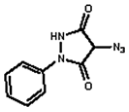
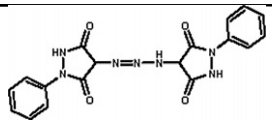
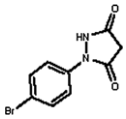
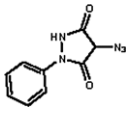
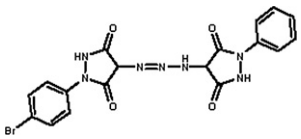
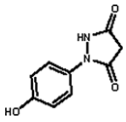
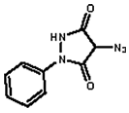
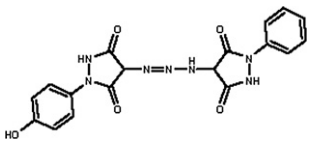
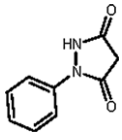
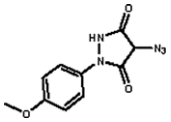
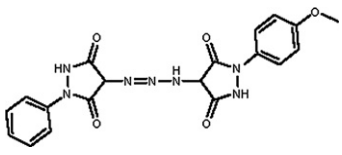
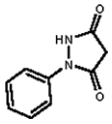
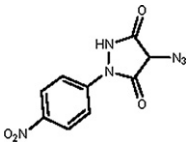
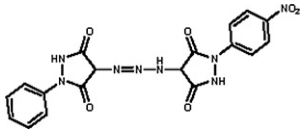
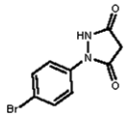
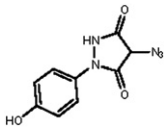
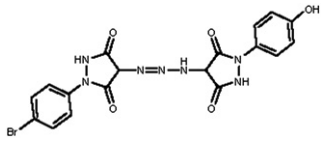
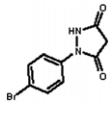
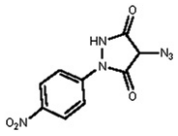
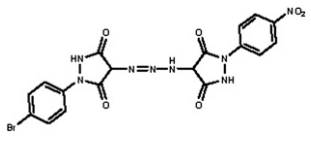
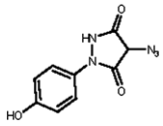
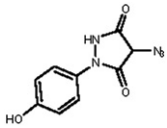
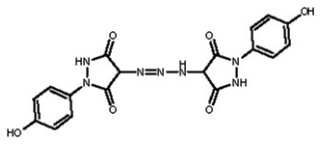
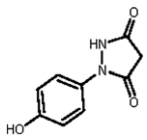
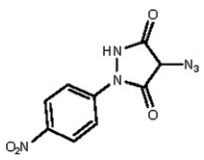
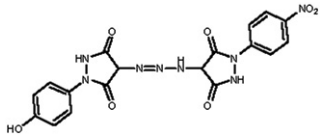
*2.4.3. 1-(4-Hydroxyl phenyl)-4-(3-(3,5-dioxo-1-phenylpyrazolidin-4-ylidene)triazylidene) pyrazolidin-3,5-dione (**4c**)*

The product **4c** was prepared according to the general procedure *C* using the following quantities: **3c** (1.43 g, 5.20 mmol), **1a** (0.92 g, 5.20 mmol) in THF (15 mL) to afford **4c** (1.85 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.42$ (s, 1H, N*H*), 8.12 (s, 2H, N*H*), 7.38–7.25 (AA′XX′ system, 4H), 7.23–6.88 (AA′XX′ system, 4H), 6.92 (m, 1H), 4.51 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.4$, 165.6, 153.9, 134.7, 132.6, 129.1, 128.3, 127.8, 126.4, 116.4 81.1, 77.5 ppm. MS (ESI): $m/z = 410.16$ $[M+1]^+$. $C_{18}H_{15}N_7O_5$ (409.11): calcd C, 52.81; H, 3.69; N, 23.95, found, C, 52.85; H, 3.73; N, 23.98.

*2.4.4. 1-(4-Methoxy phenyl)-4-(3-(3,5-dioxo-1-phenylpyrazolidin-4-ylidene) triazylidene) pyrazolidin-3,5-dione (**4d**)*

The product **4d** was prepared according to the general procedure *C* using the following quantities: **3b** (1.17 g, 5.69 mmol), **1a** (1.00 g, 5.69 mmol) in THF (15 mL) to afford **4c** (1.85 g, 99%). ^{1}H

Table 1
Structure of the synthesized triazene dyes pyrazolidin-3,5-dione based.[a]

Entry	Dyes	**1a–d**	**3a–d**	Structure of **4a–i**	Yield[b]
1	**4a**				98
2	**4b**				98
3	**4c**				98
4	**4d**				98
5	**4e**				98
6	**4f**				98
7	**4g**				98
8	**4h**				98
9	**4i**				98

[a] General reaction conditions: pyrazolidin-3,5-dione (1.0 equiv) and an organic azide (1.0 equiv), concentration of substrates = 0.3 M, solvent = THF, 25 °C.
[b] Isolated yields.

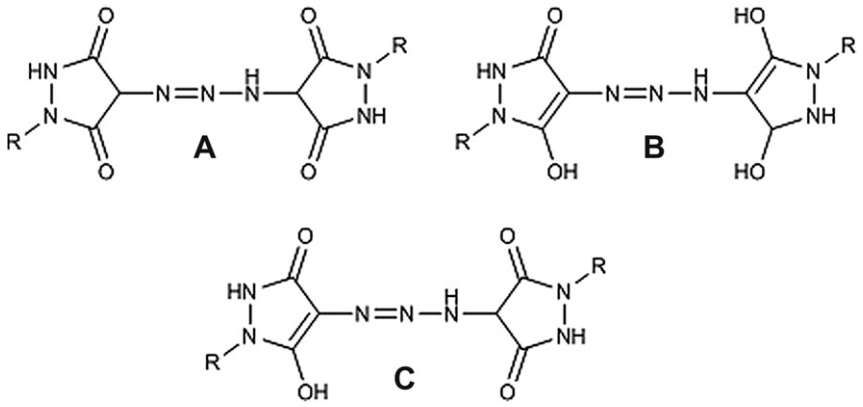


Fig. 1. Tautomeric forms of the azo-pyrazolidin-3,5-dione triazenes.

NMR (200 MHz, acetone d_6): $\delta = 12.41$ (s, 1H, N*H*), 8.12 (s, 2H, N*H*), 7.39–7.35 (AA′XX′ system, 4H), 7.29–6.92 (AA′XX′ system, 4H), 6.90 (m, 1H), 4.51 (s, 2H), 3.84 (s, 3H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.7$, 165.3, 158.8, 134.4, 132.5, 128.9, 128.2, 127.5, 125.3, 114.6 81.3, 77.8, 55.5 ppm. MS (ESI): $m/z = 424.21$ $[M+1]^+$. $C_{19}H_{17}N_7O_5$ (423.13): calcd C, 53.90; H, 4.05; N, 23.16, found, C, 53.95; H, 4.09; N, 23.19.

2.4.5. 1-(4-Nitro phenyl)-4-(3-(3,5-dioxo-1-phenylpyrazolidin-4-ylidene)triazylidene) pyrazolidin-3,5-dione (**4e**)

The product **4e** was prepared according to the general procedure *C* using the following quantities: **3d** (1.49 g, 5.69 mmol), **1a** (1.00 g, 5.69 mmol) in THF (15 mL) to afford **4e** (2.33 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.42$ (s, 1H, N*H*), 8.14 (s, 2H, N*H*), 8.11–7.08 (AA′XX′ system, 4H), 7.37–7.33 (AA′XX′ system, 4H), 6.90 (m, 1H), 4.51 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.5$, 165.1, 143.3, 140.1, 134.4, 132.6, 128.7, 127.9, 124.4, 122.6, 81.5, 77.8 ppm. MS (ESI): $m/z = 439.18$ $[M+1]^+$. $C_{18}H_{14}N_8O_6$ (438.10): calcd C, 49.32; H, 3.22; N, 25.56, found, C, 49.37; H, 3.26; N, 25.59.

2.4.6. 1-(4-Hydroxy phenyl)-4-(3-(3,5-dioxo-1-(4′-bromo) phenylpyrazolidin-4-ylidene) triazylidene) pyrazolidin-3,5-dione (**4f**)

The product **4f** was prepared according to the general procedure *C* using the following quantities: **1e** (1.00 g, 4.29 mmol), **3c** (1.18 g, 4.29 mmol) in THF (15 mL) to afford **4f** (2.08 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.41$ (s, 1H, N*H*), 8.12 (s, 2H, N*H*) 7.55–6.75 (AA′XX′ system, 4H), 7.27–6.85 (AA′XX′ system, 4H), 5.46 (s, 1H, O*H*), 4.52 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.7$, 165.6, 153.9, 135.3, 133.3, 127.5, 126.7, 126.2, 122.5, 116.5, 81.4, 77.6 ppm. MS (ESI): $m/z = 488.11$ $[M+1]^+$. $C_{18}H_{14}BrN_7O_5$ (487.02): calcd C, 44.28; H, 2.89; N, 20.08, found, C, 44.31; H, 2.92; N, 20.11.

2.4.7. 1-(4-Nitro phenyl)-4-(3-(3,5-dioxo-1-(4′-bromo) phenylpyrazolidin-4-ylidene)triazylidene) pyrazolidin-3,5-dione (**4g**)

The product **4g** was prepared according to the general procedure *C* using the following quantities: **1e** (1.00 g, 4.29 mmol), **3d** (1.14 g, 4.29 mmol) in THF (15 mL) to afford **4g** (2.20 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.41$ (s, 1H, N*H*), 8.13 (s, 2H, N*H*), 8.05–7.15 (AA′XX′ system, 4H), 7.57–6.75 (AA′XX′ system, 4H), 4.52 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.5$, 165.5, 143.6, 140.4, 135.4, 133.6, 126.9, 124.6, 122.7, 122.4, 81.6, 77.7 ppm. MS (ESI): $m/z = 517.07$ $[M+1]^+$. $C_{18}H_{13}BrN_8O_6$ (516.01): calcd C, 41.80; H, 2.53; N, 21.66, found, C, 41.84; H, 2.57; N, 21.69.

2.4.8. 1-(4-Hydroxy phenyl)-4-(3-(3,5-dioxo-1-(4′-hydroxy) phenylpyrazolidin-4-ylidene) triazylidene) pyrazolidin-3,5-dione (**4h**)

The product **4h** was prepared according to the general procedure *C* using the following quantities: **1c** (1.00 g, 5.20 mmol), **3c** (1.21 g, 4.29 mmol) in THF (15 mL) to afford **4h** (2.08 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.42$ (s, 1H, N*H*), 8.13 (s, 2H, N*H*), 7.25–6.88 (AA′XX′ system, 8H), 4.52 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.6$, 165.4, 154.2, 127.6, 126.8, 116.3, 81.4, 77.6 ppm. MS (ESI): $m/z = 426.19$ $[M+1]^+$. $C_{18}H_{13}N_7O_6$ (425.11): calcd C, 50.83; H, 3.55; N, 23.05, found, C, 50.87; H, 3.59; N, 23.09.

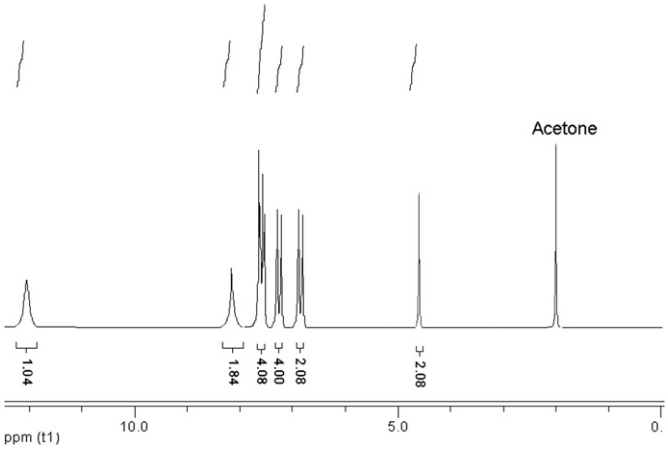


Fig. 2. ^{1}H NMR spectrum of pyrazolidin-3,5-dione triazene **4a**.

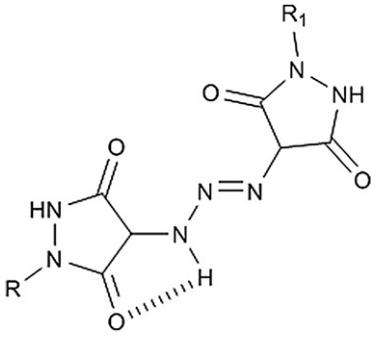


Fig. 3. Stable tautomer form of the triazene **4a**–**i**.

Table 2
Spectroscopic data of triazenes **4a**–**i**.

Dyes	^{1}H NMR		FTIR		
	N–H	Aroms-H	υ_{N-H}	υ_{Arom-H}	$\upsilon_{C=O}$
4a	12.4, 8.13	7.37 (m, 4H), 7.35 (m, 4H), 6.91(m, 2H), 4.51 (s, 2H)	3344, 3339	3045	1665
4b	12.4, 8.12	7.52 (m, 2H), 7.37–7.35 (m, 4H), 6.91–6.71 (m, 4H), 4.52 (m, 2H)	3343, 3335	3052	1663
4c	12.3, 8.12	7.38 (m, 2H), 7.25–7.23 (m, 4H), 6.91–6.88 (m, 3H), 4.51 (s, 2H)	3346, 3334	3054	1662
4d	12.4, 8.12	7.39 (m, 2H), 7.35–7.29 (m, 4H), 6.92–6.90 (m, 3H), 4.51 (s, 2H)	3347, 3335	3052	1657
4e	12.3, 8.14	8.11 (m, 2H), 7.37–7.33 (m, 4H), 7.08 (m, 2H), 6.90 (m, 1H), 4.51 (s, 2H)	3345, 3336	3051	1662
4f	12.4, 8.12	7.55 (m, 2H), 7.27 (m, 2H), 6.85–6.75 (m, 4H), 4.52 (m, 2H)	3344, 3336	3054	1653
4g	12.4, 8.13	8.05 (m, 2H), 7.57 (m, 2H), 7.15 (m, 2H), 6.75 (m, 2H), 4.52 (m, 2H)	3341, 3335	3047	1658
4h	12.4, 8.13	7.25 (m, 4H), 6.88 (m, 4H), 4.52 (m, 2H)	3346, 3338	3054	1655
4i	12.3, 8.15	8.10 (m, 2H), 7.25 (m, 2H), 7.08 (m, 2H), 6.88 (m, 2H), 4.50 (m, 2H)	3343, 3339	3057	1656

*2.4.9. 1-(4-Hydroxy phenyl)-4-(3-(3, 5-dioxo-1-(4′-nitro) phenylpyrazolidin-4-ylidene) triazylidene) pyrazolidin-3,5-dione (**4i**)*

The product **4i** was prepared according to the general procedure *C* using the following quantities: **1c** (1.00 g, 5.20 mmol), **3d** (1.36 g, 5.20 mmol) in THF (15 mL) to afford **4i** (2.35 g, 99%). ^{1}H NMR (200 MHz, acetone d_6): $\delta = 12.42$ (s, 1H, N*H*), 8.15 (s, 2H, N*H*), 8.10–7.08 (AA′XX′ system, 4H), 7.25–6.88 (AA′XX′ system, 4H), 4.50 (s, 2H) ppm. ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.7$, 165.6, 154.3, 143.3, 140.5, 127.6, 126.6, 124.2, 122.4, 116.7, 81.6, 77.8 ppm. MS (ESI): $m/z = 455.17$ $[M+1]^+$. $C_{18}H_{14}N_8O_7$ (454.10): calcd C, 47.58; H, 3.11; N, 24.66, found, C, 47.62; H, 3.14; N, 24.69.

*2.4.10. 4-(2-(2-Hydroxyphenyl) hydrazono)-1-phenyl pyrazolidin-3,5-dione (**8**)*

^{1}H NMR (200 MHz, acetone d_6): $\delta = 7.62$–7.34 (AA′XX′ system, 4H), 7.31–7.33 (m, 2H), 7.03 (s, 1H), 6.92 (m, 3H). ^{13}C NMR (50 MHz, acetone d_6): $\delta = 168.6$, 168.2, 146.4, 137.8, 136.5, 129.8, 128.5, 122.6, 122.1, 120.7, 120.1, 116.4, 115.5. MS (ESI): $m/z = 297.17$ $[M+1]^+$. $C_{15}H_{12}N_4O_3$ (296.09): calcd C, 60.81; H, 4.08; N, 18.91, found, C, 60.86; H, 4.11; N, 18.94.

*2.4.11. Azamethine **5**: 4-(3,5-dioxo-1-phenyl pyrazolidin-4-ylidene amino)-1-phenyl pyrazolidin-3,5-dione*

Bis (1-phenylpyrazolidin-3,5-dione) triazene **(4a)** (0.1 g, 0.25 mmol) was dissolved in 4 mL of toluene and heated to 150 °C for 10 h. After removal of solvent under reduced pressure, 0.09 g of the titled compound was obtained as yellow oil (50% yields). ^{1}H NMR (50 MHz, acetone d_6): $\delta = 8.11$ (s, 2H, N*H*), 7.69–7.38 (AA′XX′, 4H), 7.37–7.34 (AA′XX′, 4H), 6.92 (m, 2H), 3.9 (s, 1H). ^{13}C NMR (50 MHz, acetone d_6): $\delta = 170.4$, 168.4, 165.4, 163.8, 146.5, 137.8, 134.5, 132.1, 129.8, 128.7, 128.1, 122.4, 120.4, 80.4. MS (ESI): $m/z = 364.18$ $[M+1]^+$. $C_{18}H_{13}N_5O_4$ (363.10): calcd C, 59.50; H, 3.61; N, 19.28, found, C, 59.55; H, 3.66; N, 19.33.

*2.4.12. 4-(3,5-Dioxo-1-phenylpyrazolidin-4-ylideneamino)-1-phenylpyrazolidin-3,5-dione (**6**)*

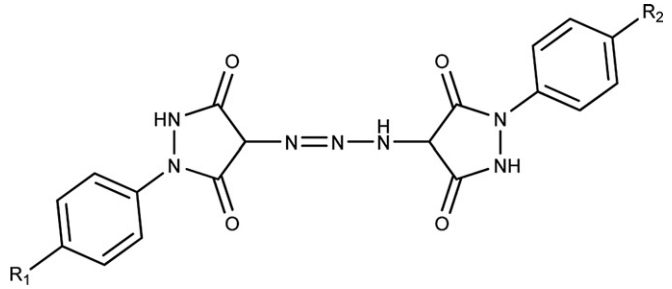
^{1}H NMR ($CDCl_3$): $\delta = 8.12$ (s, 2H, N*H*), 7.69–7.39 (AA′XX′, 4H), 7.36–7.33 (AA′XX′, 4H), 6.91 (m, 2H), 3.92 (s, 1H), ^{13}C NMR ($CDCl_3$): $\delta = 170.5$, 168.6, 165.3, 163.6, 146.2, 137.4, 134.7, 132.3, 129.7, 128.8, 128.0, 122.2, 120.6, 80.7. MS (ESI): $m/z = 365.22$ $[M+1]^+$. $C_{18}H_{13}N_5O_4$ (364.10): calcd C, 59.50; H, 3.61; N, 19.28, found, C, 59.55; H, 3.66; N, 19.31.

3. Results and discussion

3.1. Synthesis of pyrazolidin-3,5-dione azide derivatives (*AzPyr*)

The synthetic scheme of the pyrazolidin-3,5-dione azide derivatives was reported in Scheme 2. The treatment of the pyrazolidin-3,5-dione derivatives **1a**–**d** with *N*-bromosuccinimide in THF as solvent at room temperature affords the corresponding brominated derivatives **2a**–**d**. The pyrazolidin-3,5-dionyl azides **3a**–**d** were synthesized by treating **2a**–**d** with sodium azide in acetonitrile at 80 °C in high yield (99%).

Table 3
UV–vis absorbance data for pyrazolidin-3,5-dione triazenes dyes.[a]



Entry	Products	R_1	R_2	λ_{max}	Log ε[b]
1	**4a**	H	H	371	4.30
2	**4b**	Br	H	383	4.26
3	**4c**	OH	H	379	4.25
4	**4d**	H	OCH_3	408	4.21
5	**4e**	H	NO_2	461	4.44
6	**4f**	Br	OH	411	4.37
7	**4g**	Br	NO_2	459	4.61
8	**4h**	OH	OH	435	4.50
9	**4i**	OH	NO_2	477	4.58

[a] UV–vis spectra were measured in acetone at ambient temperature.
[b] ε Corresponds to the molar absorptivity with units of L mol^{-1} cm^{-1}.

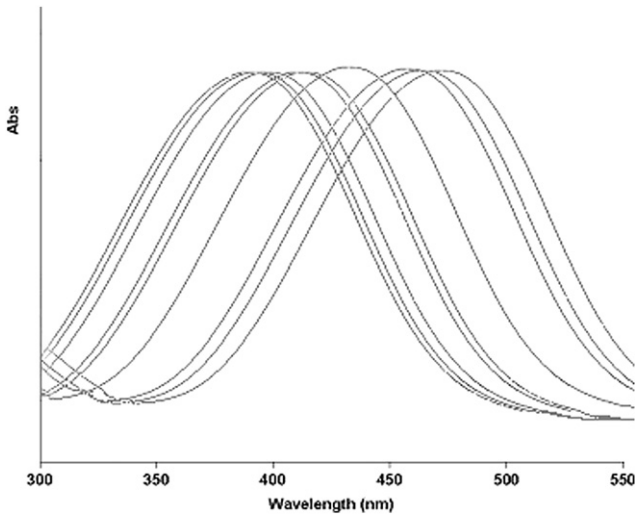


Fig. 4. UV–vis absorbance spectra of triazene **4a**–**i** compounds (from the left to the right: **4a**, **4c**, **4b**, **4d**, **4f**, **4h**, **4g**, **4e**, **4i**).

3.2. Synthesis of pyrazolidin-3,5-dione triazenes

Triazene dyes **4a**–**i** were prepared by coupling pyrazolidin-3,5-dione sodium salt, generated through deprotonation of its pyrazolidin-3,5-dione using sodium hydride (1 mol), and then isolated and used as its free **NHCPyr** with 1 mol equiv of pyrazolidin-3,5-dionyl azide (Scheme 3). The reaction was conducted at ambient temperature using tetrahydrofuran (THF) as solvent at 0.1 M substrate concentration. The purification of the resulting triazene **4a**–**i** requires only a filtration of the reaction mixture through a PTFE filter followed by evaporation of solvent. Using this work-up, triazene dyes were obtained in excellent yields (98%) and in high purity. Table 1 show the synthesized triazenes based on pyrazolidin-3,5-dione derivatives and its corresponding azides as coupling building blocks. Following the nature of the substitutes R_1 and R_2 (Scheme 3), we can assume that if the triazo linkage enabled electronic communication, a bathochromic shift should be observed by UV–vis spectroscopy as the pendent electron-donating and electron-withdrawing substituents in the resulting triazenes became more complementary. Similarly, successive downfield shifts were also expected in the NMR spectra for the same series of triazenes.

During the synthesis of triazenes **4a**–**i**, the reaction progress depended essentially on the nature of the substituents R_1 and R_2 of the pyrazolidin-3,5-dione and its azide derivatives. To obtain quantitative information on reaction progress versus time, the bimolecular rate constant of reaction involving pyrazolidin-3,5-dione derivatives and a select range of organic azides with various electronic properties were measured by ^{1}H NMR spectroscopy (in $CDCl_3$ as solvent). The coupling reaction between the free **NHCPyr** and an electron-poor azide, 4-azido-(4′-nitrophenyl) pyrazolidin-3,5-dione, was extremely fast and measured to be 0.254 L mol^{-1} s^{-1}. In contrast, the rate constant for coupling the same **NHCPyr** to relatively more electron-rich azides, 4-azido-(phenyl) and 4-azido-(4′-methoxyphenyl) pyrazolidin-3,5-dione, were relatively slow and found to be 0.05 L mol^{-1} s^{-1} and 0.02 L mol^{-1} s^{-1} respectively. Collectively, these observations were consistent with a coupling mechanism that involves nucleophilic attack of a **NHCPyr** at the terminal nitrogen of a azidopyrazolidin-3,5-dione.

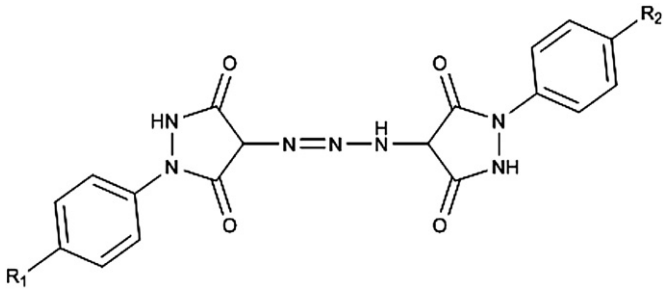
3.3. NMR spectroscopic characterization of triazenes *4a–i*

The donor–acceptor pyrazolidin-3,5-dione triazenes (**4a**–**i**) were studied by ^{1}H and ^{13}C NMR spectroscopy. In general, signals attributed to the aryl protons on the pyrazolidin-3,5-dione azide-containing moieties shifted up field whereas the aryl protons on the pyrazolidin-3,5-dione shifted downfield upon coupling. This result was consistent with charge transfer from the electron-rich component to the relatively electron-poor component. The magnitude of these shifts was strongly dependent on the nature of the substitute on the pyrazolidin-3,5-dionyl azide with a smaller dependency on the pendent functional group on the pyrazolidin-3,5-dione, although overall changes were small for all compounds studied (^{1}H NMR: <0.1 ppm; ^{13}C NMR: <1.0 ppm). The most pronounced shifts were observed in the series (^{1}H NMR, solvent = $CDCl_3$): OH–NO_2 (δ = 8.10 ppm, Ar-H ortho to NO_2; 7.09 ppm Ar-H meta to NO_2), H–NO_2 (δ = 8.15, 7.13 ppm), and Br–NO_2 (δ = 8.19, 7.18 ppm).

3.4. Tautomerism of pyrazolidin-3,5-dione triazenes *4a–i*

The symmetrical triazenes **4a** and **4h** can exist in three different possible tautomeric forms, namely the azo-keto form A, the azo-enol form B and the azo-keto-enol form **C** in Fig. 1.

Table 4
Electronic effects on triazene stability.



Entry	Products	R_1	R_2	M_p (°C)[a]	T_d (°C)[b]
1	**4a**	H	H	104	113
2	**4b**	Br	H	123	129
3	**4c**	OH	H	125	133
4	**4d**	H	OCH_3	135	127
5	**4e**	H	NO_2	145	192
6	**4f**	Br	OH	127	136
7	**4g**	Br	NO_2	148	188
8	**4h**	OH	OH	126	135
9	**4i**	OH	NO_2	148	179

[a] Melting points (M_p) are uncorrected and were determined under an atmosphere of air.
[b] Decomposition temperature (T_d) determined using thermogravimetric analysis under an atmosphere of nitrogen and defined as the temperature at which 5% mass loss occurred.

^{1}H NMR spectra of the triazenes **4a**–**i** show peaks corresponding to the aryl protons (8.17–6.88 ppm), a characteristic highly destabilized proton at 12.40 and 8.12 ppm for the hydrogen-bonded *N–H* peaks and signals in the 4–6 ppm region corresponding to the proton in position *C-4* (Fig. 2).

These NMR data prove that the hydrazo-keto tautomers form **A** is the synthesized triazene, the hydrogen borne by the –NH–N=N– bond is stabilized by the oxygen of one or both carbonyl groups present in the pyrazolidin-3,5-dione moiety (Fig. 3).

Furthermore, FTIR spectra of compounds **4a**–**i**, show *C=O* and *N–H* stretching vibrations at 3340 (*N–H* str) and at 1663 (*C=O* str), consistent with their existence in the keto-hydrazone tautomeric form **A** (Table 2).

However, the other non-symmetrical triazenes, there exist six possible forms. The formation of cyclic hydrogen bond will be strongly dependent on the nature of substituents in both benzene nuclei.

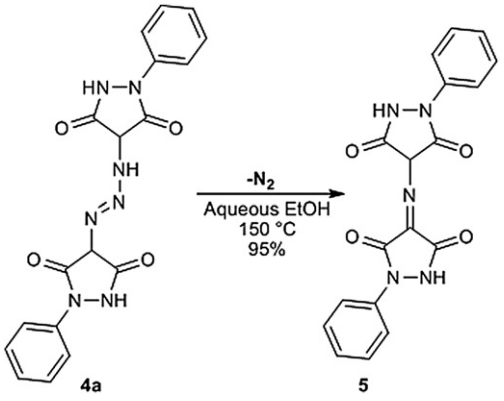


Fig. 5. Thermal decomposition of triazene via loss of nitrogen.

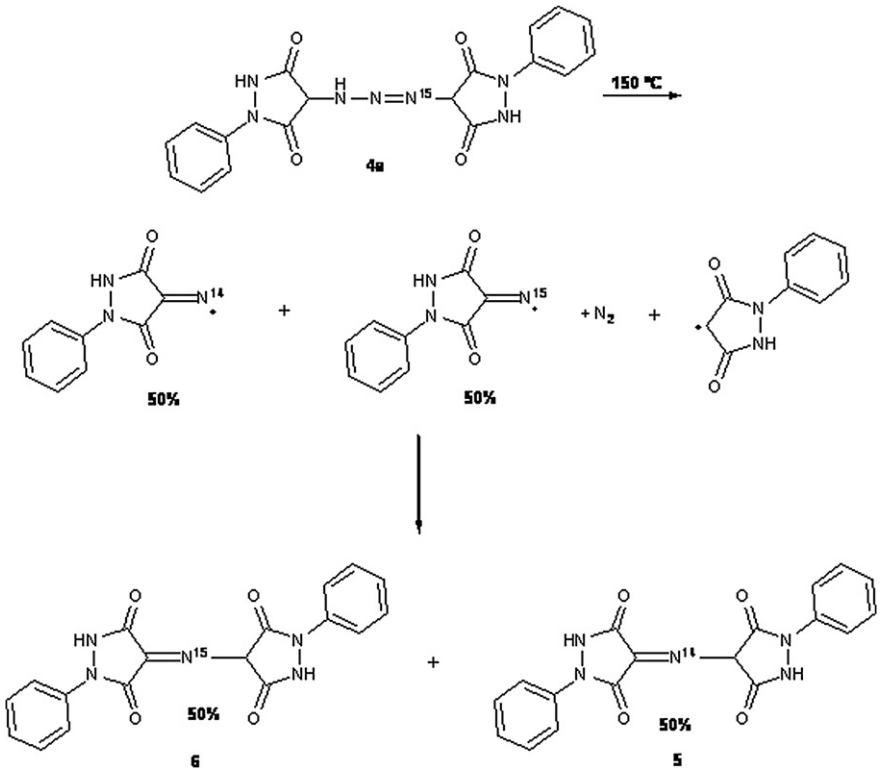
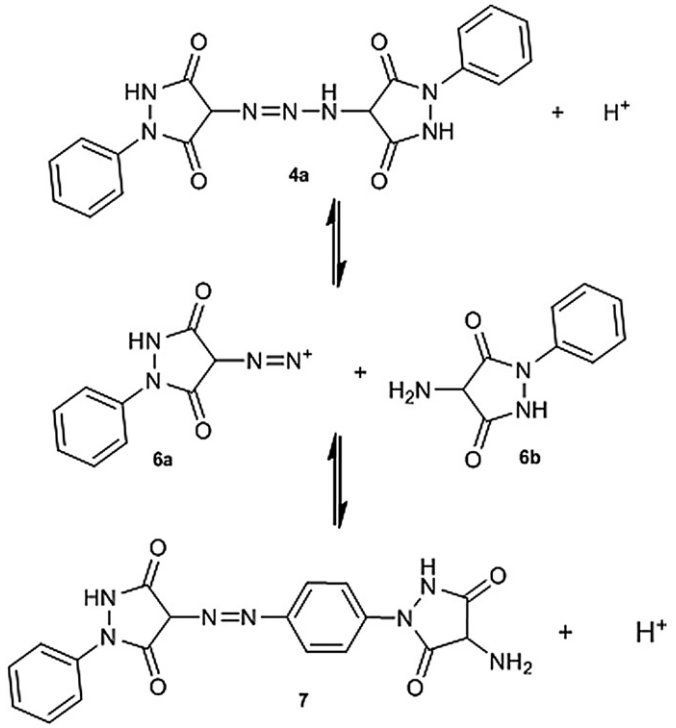


Fig. 6. Proposed mechanism of thermally triazene decomposition based on a ^{15}N-labeling experiment.

3.5. UV–vis absorption spectroscopic characterization of pyrazolidin-3,5-dione triazenes ***4a–i***

The triazene linkage (C–NH–N=N–) formed in the **NHCPyr**/**AzPyr** reaction presents structural similarities to azine (C=N–N=C) and 1,3-diene (C=C–C=C) linkages. As reported in the literature, the electronic properties of donor–acceptor azines studied by NMR spectroscopy [38–40], demonstrate that the electronic communication across the N–N bond was minimal or extensively delocalized and under some conditions exhibited nonlinear optical (NLO) responses [41]. In this sense, it is important to study the electronic properties of four-electron, conjugated π-triazene system containing three consecutive nitrogen atoms.

As shown in the UV–vis absorption spectra reported in Table 3. A gradual bathochromic shift in the λ_{max} of the triazene chromophore was observed as the electron-donating/electron-withdrawing character of its peripheral functional groups became more complementary (Fig. 4). Close analysis of the data suggested that while electronic communication between the terminal functional group on pyrazolidin-3,5-dione and the pyrazolidin-3,5-dionyl azide was observed, the interaction was relatively minor. For example, only 4–12 nm bathochromic shifts were observed in the



Scheme 4. Probable protolysis mechanism of triazene **4a**.

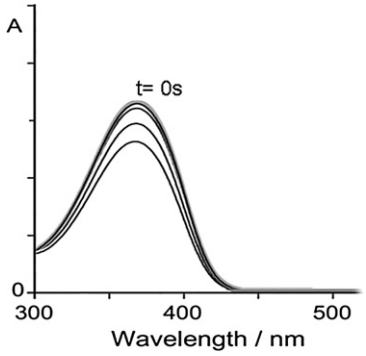


Fig. 7. Protolysis spectral of the **4a** decomposition at pH = 4, RT, intervals 1 h.

λ_{max} upon replacing one *para* hydrogens in the phenyl of pyrazolidin-3,5-dione to either hydroxyl or methoxy groups (i.e., **H**/**H** → **OH**/**H** or **Br**/**H**; entries 1–3). These observations can be explained by the high degree of bond polarization observed in the triazene formed between pyrazolidin-3,5-dione and the azide moiety, due to the strong electron-donating character of the substituents present in the pyrazolidin-3,5-dione derivatives. In contrast, significant effects on λ_{max} were observed when the terminal functional group on the pyrazolidin-3,5-dionyl azide coupling partner was varied. For example, replacing a methoxy group with a nitro group resulted in a 53 nm bathochromic shift in the λ_{max} (i.e., **H**/**OCH$_3$** → **H**/**NO$_2$**; entries 4 and 5). Similar spectroscopic changes were observed with triazenes containing electron-poor (i.e., **Br**/**OH** → **Br**/**NO$_2$**, $\Delta\lambda_{max} = 48$ nm; entries 6 and 7) and electron-rich (i.e., **OH**/**OH** → **OH**/**NO$_2$**, $\Delta\lambda_{max} = 42$ nm; entries 8 and 9) pyrazolidin-3,5-dione components. As expected, triazene OH–NO$_2$, prepared by coupling a highly electron-rich pyrazolidin-3,5-dione with a highly electron-deficient azide, exhibited the longest λ_{max} at 477 nm for any of the triazenes studied (entry 9). Collectively, these results suggested that the triazeno linkages (C–NH–N=N–) were effective in delocalizing electronic charge between complementary **NHCPyr** and organic azide components.

3.6. Thermogravimetric analysis of triazene *4a–i*

The thermal stability of triazenes **4a**–**i** has been studied in the solid-state using thermogravimetric analysis to investigate how the size of the substituents (R_1 and R_2) as well as electronic effects of the pyrazolidin-3,5-dione component affect triazene stability. The thermal stabilities of various triazenes evaluated in the solid-state using thermogravimetric analysis (TGA) are illustrated in Table 4. The results show that the material suffers thermal degradation at temperatures above about 110 °C.

Following the results reported in Table 4, for example the T_g of the triazene **4e** which possessed an electron-deficient *p*-nitro substitute decomposes at 192 °C (entry 5), and was 65 °C higher than an analog containing a *p*-methoxy substitute **4d** ($T_g = 127$ °C, entry 4). We can conclude that increasing the size of the substitute positively influenced triazene stability. The role of pyrazolidin-3,5-dione electronics in influencing triazene thermal stability was found to be relatively major. These results suggested that coupling pyrazolidin-3,5-dione possessing phenyl substituents with electron deficiency affords triazenes with the highest thermal stabilities. Melting points (M_p) were also determined and found to be below the decomposition temperature (T_d) for all compounds studied.

3.7. Thermo analysis stability of triazenes *4a–i*

To determine the thermal decomposition process of the triazenes synthesized in this study, **4a** was heated to 150 °C in aqueous ethanol for 90 min, the azamethine (**5**) has been observed by ^{1}H NMR spectroscopy and isolated in 50% yield via flash chromatography. The difference between the molecular weight of the triazene **4a** and the azamethine (**5**) was 28 Da which corresponds to the molecular weight of the molecular nitrogen (Fig. 5).

It is reported in the literature that aromatic triazenes decompose thermally via radical intermediate following breakage of the N^2–N^3 bond [42]. To confirm this hypothesis, pyrazolidin-3,5-dionyl azides containing an isotopically enriched nitrogen atom has been synthesized using ^{15}N-labeled sodium azide. After, this ^{15}N-labeled azide has been coupled with pyrazolidin-3,5-dione **1a** and the resulting ^{15}N-labeled triazene **4a** was heated to 150 °C in aqueous ethanol. The resulting azamethine **6** was obtained in 50% yield and it was characterized by mass spectrometry. On the basis

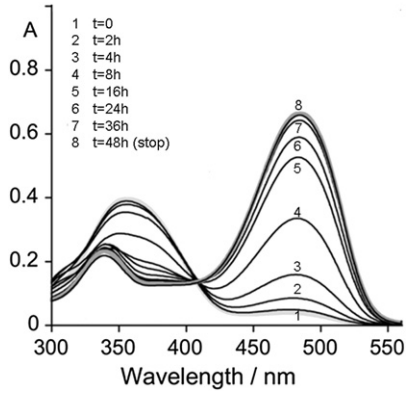


Fig. 8. Spectral record of the decomposition of triazene **4a** in HCl, pH 4 in the presence of phenol in large excess at room temperature.

of these results, we suggest the following thermal decomposition mechanism of triazene **4a** as shown in Fig. 6.

Interesting observation was that the addition of HCl solution (1 N) in the aqueous solution of ethanol (10/1) reduced the time of decomposition of triazene **4a** from 90 min to 30 min. Therefore we found it necessary to study the stability of the triazene **4a**–**i** in acidic media.

3.8. Protolysis of triazenes dyes *4a–i*

The azo coupling reaction at nitrogen takes place in neutral to weakly alkaline media [16]. In acidic media, the azo coupling reaction at nitrogen is reversible, therefore the triazenes are not stable in acidic medium. Triazenes are protonated by acid at the amino group and decompose back to the aniline and diazonium ion [43–45]. This cleavage may be followed by azo coupling reaction in the nucleus of the aniline derivatives formed (Scheme 4).

Typically, experiments were carried out in buffer–ethanol mixtures in the presence of 5-fold concentration of HCl compared to the initial concentration of triazene (5×10^{-5} M). The decrease of triazene with time was measured at room temperature in different buffer solutions. A characteristic example for a protolysis experiment followed by UV–visible spectra measurements are reported in Fig. 7.

The protolysis UV–vis spectra reported in Fig. 7 show firstly a very slow decrease in the absorbance of the absorption band at $\lambda_{max} = 371$ nm. If the decomposition of the triazene **4a** in the presence of HCl solution at pH = 4 affords the diazonium salt **6a**, it is very probable that this diazonium salt reacts with an

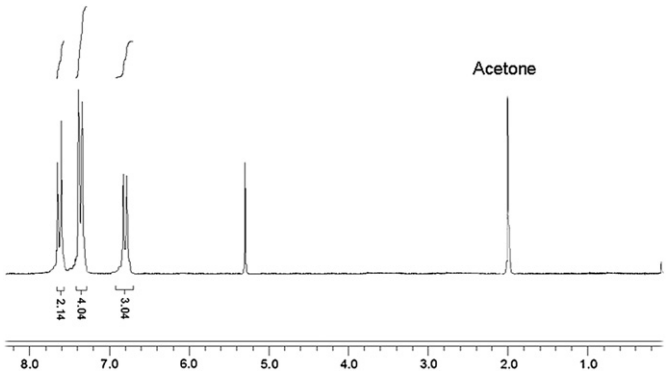


Fig. 9. ^{1}H NMR spectrum of the protolysis resulting azo dye 8.

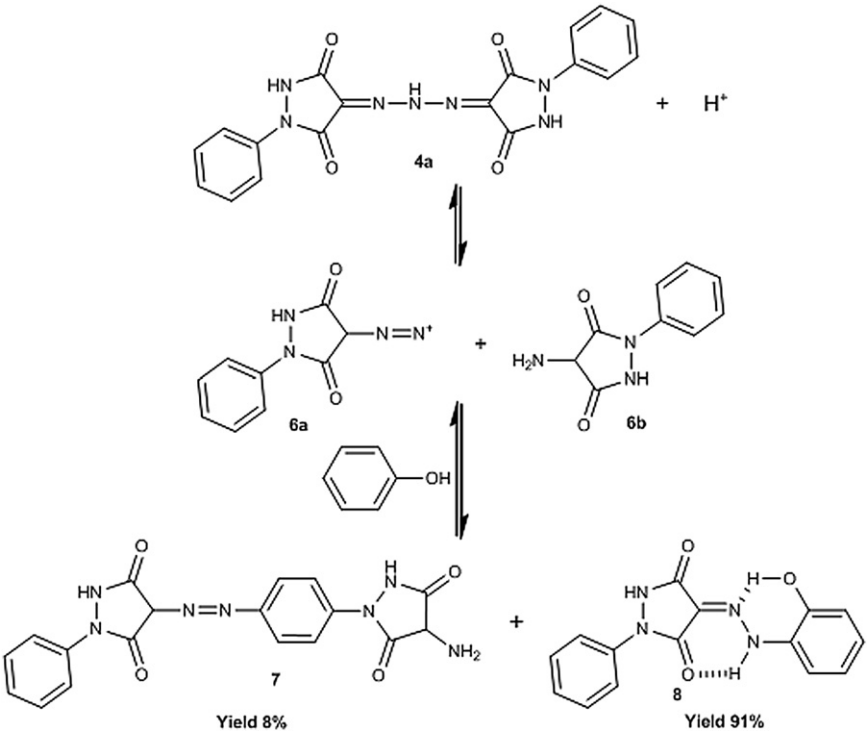


Fig. 10. Protolysis of **4a** in the presence of HCl (pH 4) and a large excess of phenol.

electrophilic site to form its corresponding azo dye. Therefore, the protolysis UV–vis spectra of triazene **4a** at pH 4 in the presence of a phenol will lead to a decrease in the absorbance at $\lambda_{max} = 371$ and an increasing of a new band which corresponds to the formed azo dye. For this purpose and to confirm that the absorbance decrease of the triazene **4a** is due to its reverse decomposition to the diazonium ion **6a** and 4-amino-1-phenyl, pyrazolidin-3,5-dione **6b** (Scheme 4), the same experiment was carried out in the presence of phenol in a large excess. We have found that the decrease in absorbance at the triazene $\lambda_{max} = 371$ nm is accompanied by an increase in absorbance at $\lambda_{max} = 446$ nm, the spectra intersecting at an isosbestic point (Fig. 8).

To characterize the formed dye after the protolysis of the triazene **4a** at pH 4, the dye corresponding to the absorbance band at $\lambda_{max} = 446$ nm have been isolated by flash chromatography (AcOEt/PE: 10/3, $R_f = 0.53$) and characterized by ^{1}H NMR spectroscopy (Fig. 9).

The ^{1}H NMR spectrum reported in Fig. 9 indicates that the isolated compound resulting from the protolysis of the triazene **4a** in the presence of HCl (pH 4) in an a large excess of phenol corresponds to the azo dye 8 and not its *para*-isomer because of the hydrogen of the phenol is stabilized by an intramolecular H-bond with the nitrogen of the azo bond which explains the absence of the *–OH* signal on the ^{1}H NMR spectrum (Fig. 10).

To explain the very slow decrease in the absorbance of the absorption band at $\lambda_{max} = 371$ nm observed when 4a was treated with HCl (pH 4), we have attempted to synthesize dye 7 by coupling of 4-amino-1-phenyl pyrazolidin-3,5-dione **6b** with itself in the presence of $NaNO_2$ in HCl/H_2O: 1/10 as solvent. We have found that the dye 7 (Fig. 10) was synthesized but in 8% as yield. However, its isomer, the triazene **4a**, was obtained in 91% as yield. As reported in Fig. 3, the major formation of triazene **4a** may be due to the existence of intramolecular hydrogen bonds in **4a** between the =N–*N*–*H*–N= bond which is stabilized by the oxygen of one of both carbonyl groups present in the pyrazolidin-3,5-dione moiety, and its absence in the azo derivative 7 which favors the coupling between the diazonium salt **6a** and the amine formed **6b**.

4. Conclusions

A novel class of pyrazolidin-3,5-dione triazenes have been prepared by coupling *N*-heterocyclic pyrazolidin-3,5-dione **NHCPyr** with various pyrazolidin-3,5-dionyl azides in excellent yields (98%). The structure of these triazenes were confirmed by UV–vis spectroscopy, NMR spectroscopy, mass spectroscopy and thermogravimetric analysis. The electronic properties of the new triazene dyes were dominated by the substituent nature of the coupled **NHCPyr** and **AzPyr** and its complementarities in the formed triazene dye. Triazene thermal stability was found to be also governed by the electronic substituent nature of the pyrazolidin-3,5-dione moiety in particular, a pyrazolidin-3,5-dione triazene possessing an electron-deficient phenyl substituent affords triazenes with the highest thermal stability. The decomposition mechanism was also suggested by using an isotopically labeled azide and found to afford molecular nitrogen and an azamethine as thermal decomposition product. The protolysis in acidic environment of triazene **4a** shows that these dyes are stable in the presence of a strong acid. This acidic stability is due to the existence of intramolecular hydrogen bonds in **4a** between the =N–*N*–*H*–N= bond which is stabilized by the oxygen of one of both carbonyl groups present in the pyrazolidin-3,5-dione moiety, and its absence in the corresponding azo derivative which favor the formation of the triazene dye and not its corresponding azo dye.

Acknowledgments

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