Interplay of dual reactivity in the reaction of pentafulvenes with 1,2,4-triazoline-3,5-diones: experimental and theoretical investigations†‡

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A detailed investigation on the reaction of pentafulvenes with *N*-substituted-1,2,4-triazoline-3,5-diones leading to the formation of five- and seven-membered azapolycycles is described. The observed reactivity is explained based on the electronic and frontier molecular orbital features of pentafulvene and triazoline dione, which suggested that the latter molecule can add to the former one *via* a [4 + 2] cycloaddition or it can undergo a nucleophilic reaction at the exo carbon atom of pentafulvene. These reactions would ultimately give the same product and the energetics of them suggested that both mechanisms are operative in the reaction conditions.

Introduction

The non-functionalized carbon–carbon multiple bond systems are recognized as latent functional groups; however they are generally unreactive towards carbon nucleophiles due to their electron rich π-orbitals. Fulvenes, cyclic molecules with odd number of carbon atoms in the ring belong to the category of non-functionalized carbon–carbon double bonds.[1] According to the size of the ring skeleton, they are named as triafulvenes, pentafulvenes, heptafulvenes, nonafulvenes *etc*. (Fig. 1). Fulvenes possess a particular type of polar system that features an unconventional structure with a unique carbon–carbon double bond. Based on their dipole moments and as well as on their reactivity patterns, fulvenes would occupy an intermediate position between the open-chain olefinic and aromatic compounds.

Among various fulvenes, pentafulvenes represent a very attractive structural unit, not only as a model for theoretical studies, but also as a valuable building block to access polycyclic cyclopentanoids through a diverse array of cyclizations.[2] Designing efficient short routes for the stereoselective construction of polycyclic molecules is currently one of the main challenges in synthetic organic chemistry. Pentafulvenes have been the subject of great interest both from the synthetic and theoretical point because they exhibit different modes of cycloadditions. In cycloadditions, pentafulvenes can participate as a 2π, 4π or 6π component[3] and have served as excellent synthons for the synthesis of triquinanes, pyrindines *etc*. Investigations from our own laboratory have unravelled the interesting reactivity profile of fulvenes in cycloaddition reactions.[4]

N-Substituted-1,2,4-triazoline-3,5-dione on the other hand is a reactive dienophile. It undergoes smooth Diels–Alder reaction with conjugated dienes,[5] while with various olefins, it undergoes ene reaction.[6] Reports indicate that it can also undergo [2 + 2] cycloaddition with certain olefins leading to the formation of 1,2-azetidines.[7] A survey of literature showed that there is only scant information[8] available on the reaction of 1,2,4-triazoline-3,5-dione with fulvenes. To the best of our knowledge, there is no report on the theoretical interpretation of the observed reactivity of fulvenes with 1,2,4-triazoline-3,5-diones. As part of our interest in the chemistry of pentafulvenes,[4d–f] we undertook a detailed investigation of the reaction of various pentafulvenes with *N*-substituted-1,2,4-triazoline-3,5-diones. The observed reactivity has been rationalized based on theoretical calculations. Our results are discussed in the following section.

Results and discussion

Our studies were initiated with the reaction of 6,6-diphenylfulvene **A** with *N*-phenyl-1,2,4-triazoline-3,5-dione **B**. The reaction proceeded smoothly affording a mixture of azapolycycles **1a** and **1b** (1 : 1.2) in 81% yield (Scheme 1).

The structural formulae of **1a** and **1b** were assigned based on spectral analysis and by comparison to the literature report. In ^{1}H NMR spectrum of **1a**, the olefinic protons resonated as a double doublet at δ 6.26 ppm (J = 2.8, 5.6 Hz) and a doublet

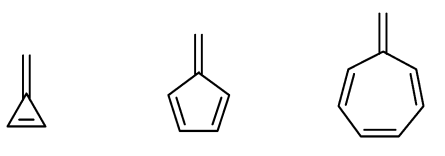

Fig. 1 Different types of fulvenes.

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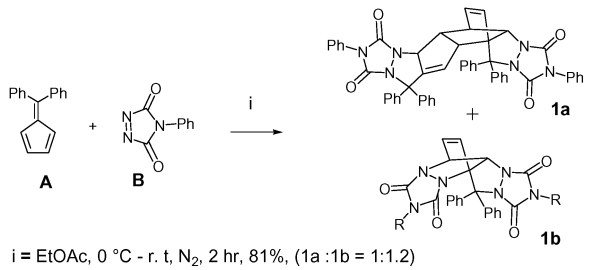
† Dedicated with respect to Dr G. Vijay Nair on the occasion his 65th birthday.
‡ The HTML version of this article has been enhanced with colour images.



i = EtOAc, 0 °C - r. t, N_2, 2 hr, 81%, (1a :1b = 1:1.2)

Scheme 1

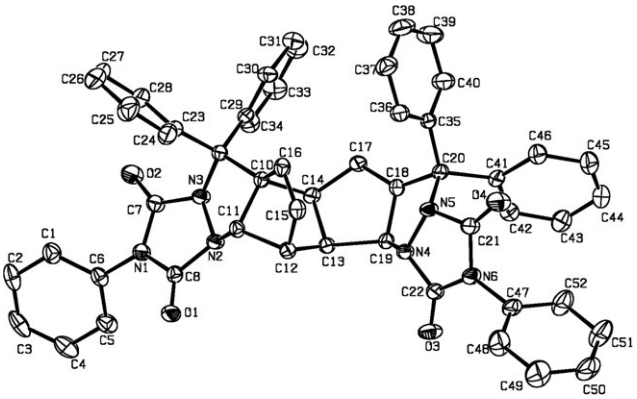


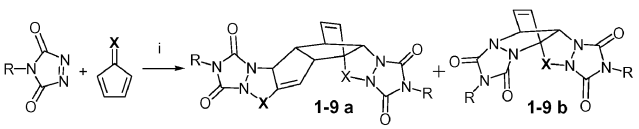
Fig. 2 ORTEP diagram of compound **1a** with atom numbering scheme (40% probability factor for the thermal ellipsoids; hydrogen atoms are omitted for clarity).

at δ 5.87 ppm (J = 5.8 Hz). In the ^{13}C NMR spectrum the characteristic carbonyl carbons of the urazole moieties resonated at 152.9, 150.7, 150.2 and 149.1 ppm, respectively. High-resolution mass spectral analysis also supported the assigned structure. Further, the structure of **1a** was unambiguously confirmed by single crystal X-ray analysis (Fig. 2).

In ^{1}H NMR spectrum of **1b**, the olefinic protons appeared as a doublet (δ 7.03 ppm) and a multiplet (δ 6.46 ppm). The protons on the carbon adjacent to the urazole nitrogens were observed as singlets at δ 5.56 ppm and δ 4.73 ppm, respectively. The four carbonyl carbons resonated at 157.4, 155.7, 150.2 and 149.5 ppm, respectively in the ^{13}C NMR spectrum. The reaction in Scheme 1 was repeated with various pentafulvenes and *N*-substituted-1,2,4-triazoline-3,5-dione. The results are summarized in Table 1. The reaction of one equivalent of fulvene with two equivalents of 1,2,4-triazoline-3,5-dione at 0 °C afforded a separable mixture of five- and seven-membered azapolycycles. In some cases (entries 5 and 7, Table 1) only the 1 : 2 adducts were observed (**5b** and **7b**, respectively).

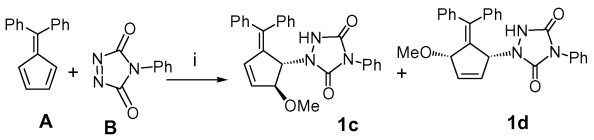
The reaction was carried out in different stoichiometric ratios of the substrates, but poor results were obtained. For example when we repeated the reaction with highest yield,

Table 1 Reaction of 1,2,4-triazoline-3,5-diones with pentafulvenes[a]



Entry	R	X	Products (**a** : **b**)	Yield (%)
1	Ph	CPh_2	**1a** + **1b** (1 : 1.2)	81
2	Ph		**2a** + **2b** (2.4 : 1)	81
3	Ph		**3a** + **3b** (1 : 2)	62
4	CH_2Ph		**4a** + **4b** (1 : 2)	86
5	CH_2Ph		**5b**	77[b]
6	CH_2Ph	CPh_2	**6a** + **6b** (1 : 2)	92
7	$CH_2C_6H_4Me$-*p*	CPh_2	**7b**	78[b]
8	$CH_2C_6H_4Me$-*p*		**8a** + **8b** (2.1 : 1)	85
9		CPh_2	**9a** + **9b** (1.7 : 1)	61

[a] i = TAD (2 equiv.). fulvene (1 equiv.), ethyl acetate (20 ml), 0 °C to r.t., N_2, 2 h. [b] **5a** and **7a** not formed.



i = MeOH/CH_2Cl_2 , -40 °C-r.t, N_2, 2 hr, 67%, (1c :1d = 2.2:1)

Scheme 2

(entry 6, Table 1), with 6,6′-diphenylfulvene and 4-benzyl-1,2,4-triazoline-3,5-dione, in 1 : 1 ratio under the same reaction conditions, afforded 10% of **6a** and 16% of **6b**. The reaction of two equivalents of fulvene with one equivalent of triazolinedione afforded only dimerized product **6a** (15%) along with 40% of unreacted fulvene. The monoadduct was not isolated in any of the experiments.

The trapping of the reactive intermediates with methanol was carried out to support the zwitterionic mechanism.[8] In an initial experiment we performed the cycloaddition between fulvene **A** and TAD **B** in a dichloromethane–methanol (1 : 5) mixture at −40 °C. The reaction afforded a separable mixture of methanol trapped products **1c** (46%) and **1d** (21%), (Scheme 2). The structures of the products **1c** and **1d** were assigned based on spectroscopic data and by comparison with literature.[8]

The presence of the olefinic functionality and the urazole nitrogen makes these azapolycycles potentially useful for the introduction of diverse functionality. The present synthetic methodology involves simple reaction steps leading to highly functionalized azapolycycles in excellent yield.

Geometric and electronic features of pentafulvene and triazolinedione

The 6π electron system of pentafulvene is isoelectronic to benzene. The latter is well known for its aromatic stabilization of around 30 kcal mol^{-1} arising from 6π-electron cyclic delocalization.[9] On the other hand, pentafulvene is susceptible toward addition reactions and it is found to be 27 kcal mol^{-1} less stable than benzene at B3LYP/6-31G* level of theory. The optimized geometry of pentafulvene is depicted in Fig. 3(a), which shows the two localized double bonds of length 1.353 Å each in the ring and another one of 1.344 Å in the exo position. The exo double bond is more localized than the ring double bonds, which is consistent with the experimental geometry.[10] Though this bond length distribution implies that the exo bond is more reactive for addition reaction than the ring double bonds, we see that the molecular electrostatic potential (MESP) distribution of this molecule is supportive of high reactivity of the ring double bonds.

In Fig. 3(a) and (b), the electronic feature of fulvene is depicted *via* its MESP. The more localized nature of the C1–C2, C3–C4 and C5–C6 bonds can be seen *via* MESP as it shows minima over the mid-point region of those bonds. The MESP minima over the ring double bonds are 58% more negative than the MESP minimum over the exo double bond. This feature is contradictory to their bond lengths because the exo bond C5–C6 is the shortest and one would expect more

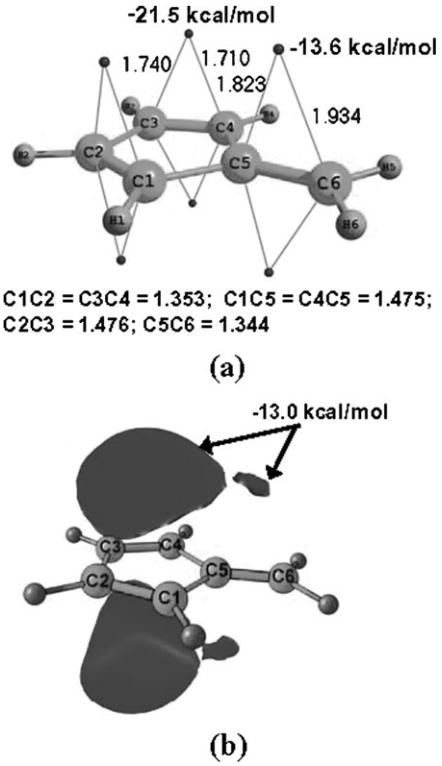


Fig. 3 (a) MESP minima (V_{min}) over the mid-point region of double bonds. (b) The electronic features of fulvene visualized *via* the MESP isosurface of value −13.0 kcal mol^{-1}. Distances in Å.

electron rich character to this bond. This significant difference in the electron distribution can be attributed to the tendency of the 4π-electron conjugation over C1, C2, C3 and C4 to acquire more electron density from the C5–C6 π-bond, in order to decrease the 4*n* electron antiaromatic destabilization within the ring. This suggests electron deficient character to C6, and this atom is 1.973 Å away from the nearest MESP minimum (V_{min}). The (V_{min}) with value −21.5 kcal mol^{-1} is closer to C1 and C4 atoms, suggesting higher reactivity to these atoms. Therefore, in cycloaddition reactions, the electron rich C1C2C3C4 unit would act as the diene part with probable cycloadduct connectivity at C1 and C4 atoms. On the other hand, the substantial reduction in the electron density over the exo bond suggests that this carbon is also susceptible for a nucleophilic attack.

In the case of triazolinedione, a short N1–N2 bond (1.243 Å) is connected to two long bonds N1–C8 (1.505 Å) and N2–C7 (1.505 Å) and this suggests a highly localized N–N bond (Fig. 4(a)). On the other hand, the O1C8N3C7O2 π-region is more delocalized due to a 6π-electron linear conjugation through the planar N3 atom. Therefore, the N1 and N2 atoms appeared to be more electron rich in comparison with the more electronegative oxygen atoms.

This feature is easily seen through the (V_{min}) as it shows a value of −33.8 kcal mol^{-1} for the lone pair region of N1 and N2 as compared to a value of −29.1 kcal mol^{-1} for the oxygen atoms. The MESP distribution shown in Fig. 4(b) suggests that the peripheral region of the molecule in the molecular plane, particularly in the lone pair direction of N1 and N2,

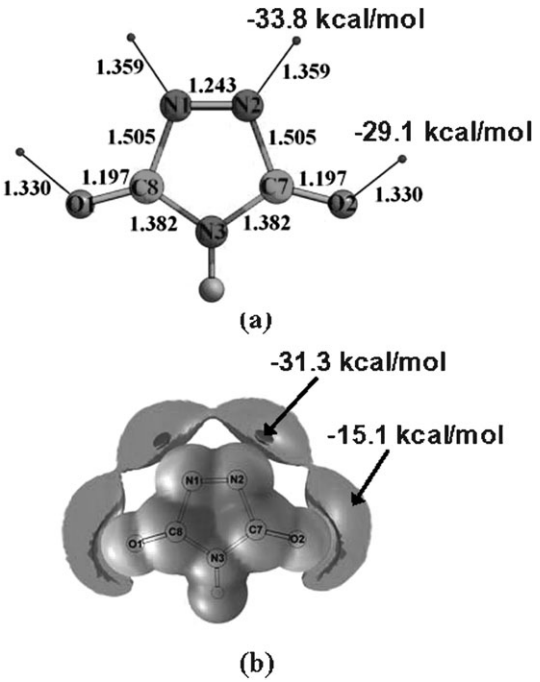


Fig. 4 (a) Geometry of triazolinedione (bond lengths in Å) along with its V_{min} values (small gray dots, shown as blue in HTML version‡). (b) MESP isosurfaces and MESP mapped on atom spheres. The central region (red in HTML version‡) has positive MESP.

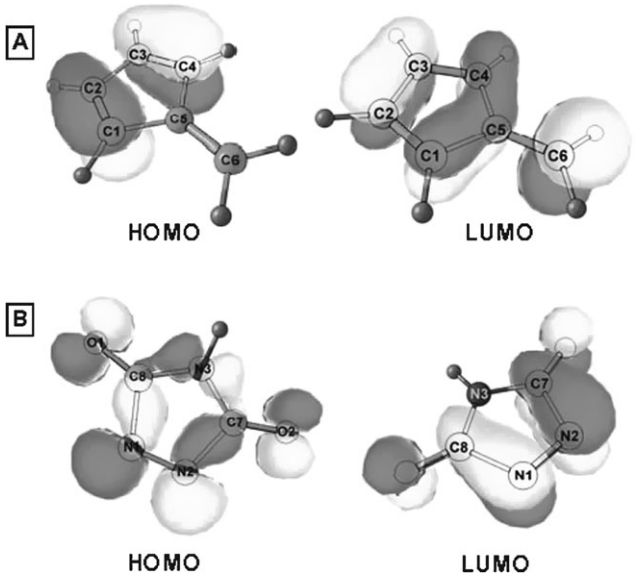


Fig. 5 Frontier molecular orbitals of (A) fulvene and (B) triazolinedione.

except that along the N3–H bond is electron rich as compared to the π faces of the molecule. So triazolinedione might show strong nucleophilic character for N1 and N2 atoms. On the other hand, considering the localized nature of N1–N2 bond and electron deficient nature of the π-faces, it might also show π-bond reactivity of the N1–N2 bond for cycloaddition by acting as a dienophile.

Thus the MESP analysis of both pentafulvene and triazolinedione support dual reactivity to them, *viz*. the reactivity for a cycloaddition and reactivity for a nucleophilic reaction. The frontier molecular orbitals (FMO) of these molecules depicted in Fig. 5 are also in support of their dual reactivity. For instance, the HOMO of fulvene and LUMO of triazolinedione are in perfect agreement for a [4 + 2] cycloaddition leading to C1–N1 and C4–N2 bond formation. Similarly, the vacant p orbital on the exocyclic C6 atom (LUMO) is susceptible for a nucleophilic attack by the N1 or N2 lone pair orbital (HOMO of triazolinedione).

Energetics of [4 +2] cycloaddition and nucleophilic reaction

As expected from the MESP analysis, the more reactive carbon atoms C1 and C4 interact with the N=N double bond of the triazolinedione in the transition state (TS) for a [4 + 2] cycloaddition (Fig. 6). The **TS1** thus formed is found to be unsymmetric as it showed C1–N1 = 1.877 Å and C4–N2 = 2.631 Å. The activation energy based on only the total electronic energy (E_{act}) was found to be 5.9 kcal mol^{-1}. However, an entropy factor is important in intermolecular cycloaddition reactions and after including the entropy correction, the free energy of activation (G_{act}) turned out to be 20.4 kcal mol^{-1}. The product **1** formed in this step of the reaction is nearly at the same free energy level as that of the reactant systems.

Product **1** is not the most stable structure, and in the next step with G_{act} of 18.1 kcal mol^{-1}, the C4–N2 bond breaks as it passes through **TS2** yielding the intermediate zwitterion **2**. In the subsequent step, the N2 atom of the zwitterion migrates to the C6 atom of the exocyclic π-bond *via* **TS3** giving the most stable product **3** at a relative free energy of −13.2 kcal mol^{-1} (relative with respect to the sum of the free energies of pentafulvene and triazolinedione). Since during the conversion of **1** to **3**, the C4–N2 bond and exocyclic C5–C6 π-bond are broken and a new C6–N2 bond is formed, this part of the reaction can be considered as the migratory insertion of the C–N bond to the exocyclic π-bond. It may be noted that when **TS1** is formed, the π-face of the triazolinedione is away from the exocyclic π-bond. Triazolinedione can also approach the fulvene so that the π-face of it can be at the same side of the exocyclic π-bond. For such an orientation, a **TS** located for the cycloaddition product similar to **1** was 6.5 kcal mol^{-1} higher in energy than **TS1**. So the reaction pathway depicted in Fig. 6 is the preferred one.

We have also probed for a nucleophilic reaction mechanism. According to this mechanism shown in Fig. 7, at first the lone pair on the N–N double bond interacts with the electron deficient exocyclic carbon. The G_{act} of 22.5 kcal mol^{-1} obtained from **TS4** is comparable to the rate determining step of the cycloaddition mechanism (20.4 kcal mol^{-1}). The zwitterionic intermediate **4** thus formed will be quickly converted to the product **3** *via* **TS5** because this second step required only a G_{act} of 8.8 kcal mol^{-1}.

When we compare the [4 + 2] cycloaddition and the nucleophilic reaction mechanism, we suggest the former mechanism as the dominant one because of its slightly lower G_{act}

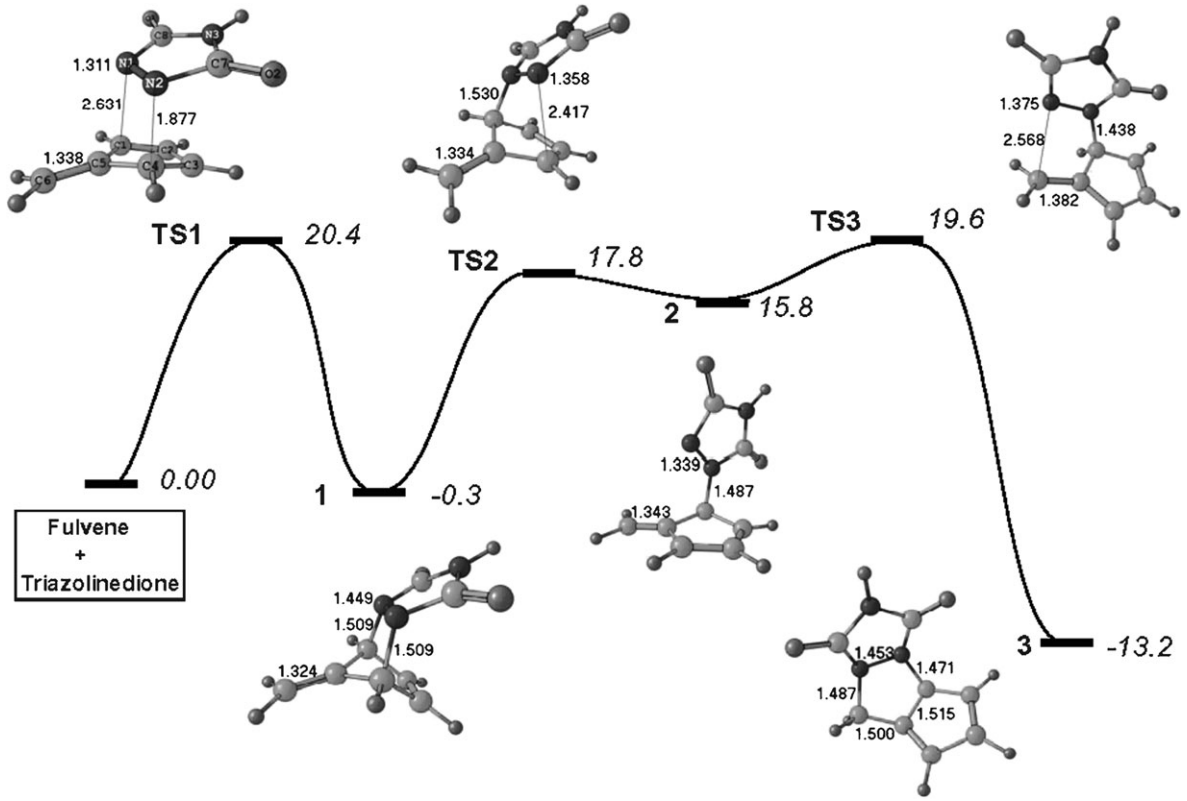


Fig. 6 Free energy profile for the cycloaddition reaction between pentafulvene and triazolinedione, and subsequent migratory insertion reaction. Values in square brackets are the corresponding enthalpy change. Distances in Å and energies in kcal mol^{-1}.

as compared to the latter one. However, the two-step process of the nucleophilic mechanism is also attractive. Moreover, the G_{act} of 22.5 kcal mol^{-1} obtained for the first step of nucleophilic mechanism and its overall G_{act} of 23.6 kcal mol^{-1} is within the achievable limit of a feasible reaction. Therefore, it is felt that both cycloaddition and nucleophilic reaction mechanisms are operative in the reaction.

Once, **3** is formed, the formation of products **1a** and **1b** given in Scheme 1 is easy to explain. **1b** is the result of the [4 + 2] cycloaddition between the cyclopentadiene unit in **3** and the N=N double bond of another triazolinedione molecule. Similarly, **1a** is formed when C–C coupling *via* [4 + 2] cycloaddition occurs between two molecules of **3** at their cyclopentadiene unit.

Conclusions

The electronic and frontier molecular orbital features of pentafulvene and triazolinedione suggest that the latter molecule can add to the former one *via* a [4 + 2] cycloaddition at electron rich 3,4 positions of the pentafulvene or by a nucleophilic reaction at the electron deficient exo carbon atom. These reactions would ultimately give the same product and the energetics of them suggests that both mechanisms are operative in the reaction conditions. The products, seven- and five-membered azapolycycles are novel molecules which can be used as efficient scaffolds in the design of new macrocycles. Reports by Ma and Dougherty,[11] Nolte and co-workers[12] and others[13] show that the rigid polycyclic molecules with heteroatoms can function as efficient receptors for various substrates. The rigid azapolycycles discussed in this manuscript are potentially amenable to a number of synthetic transformations and can be efficiently utilized in the design and synthesis of novel macrocycles with molecular recognition properties. Further work along this line is in progress and will be reported in due course.

Experimental

General

All reactions were carried out in oven-dried glassware under nitrogen atmosphere. Progress of the reaction was monitored by thin layer chromatography, which was performed on Merck precoated plates (silica gel, 60 F_{254}, 0.25 mm) and was visualized by fluorescence quenching under UV light or by staining with Enholm yellow solution. Column chromatography was done using 100–200 mesh silica gel and an appropriate mixture of petroleum ether (60–80 °C) and ethyl acetate for elution. The solvents were removed using a Buchi rotary evaporator. The IR spectra were recorded on Nicolet FT-IR spectrometer. NMR spectra were recorded on Bruker FT-NMR spectrometer using $CDCl_3$ or a $CDCl_3$–CCl_4 mixture (7 : 3) as solvent. TMS was used as internal standard and chemical shifts are in the δ-scale. High-resolution mass spectra

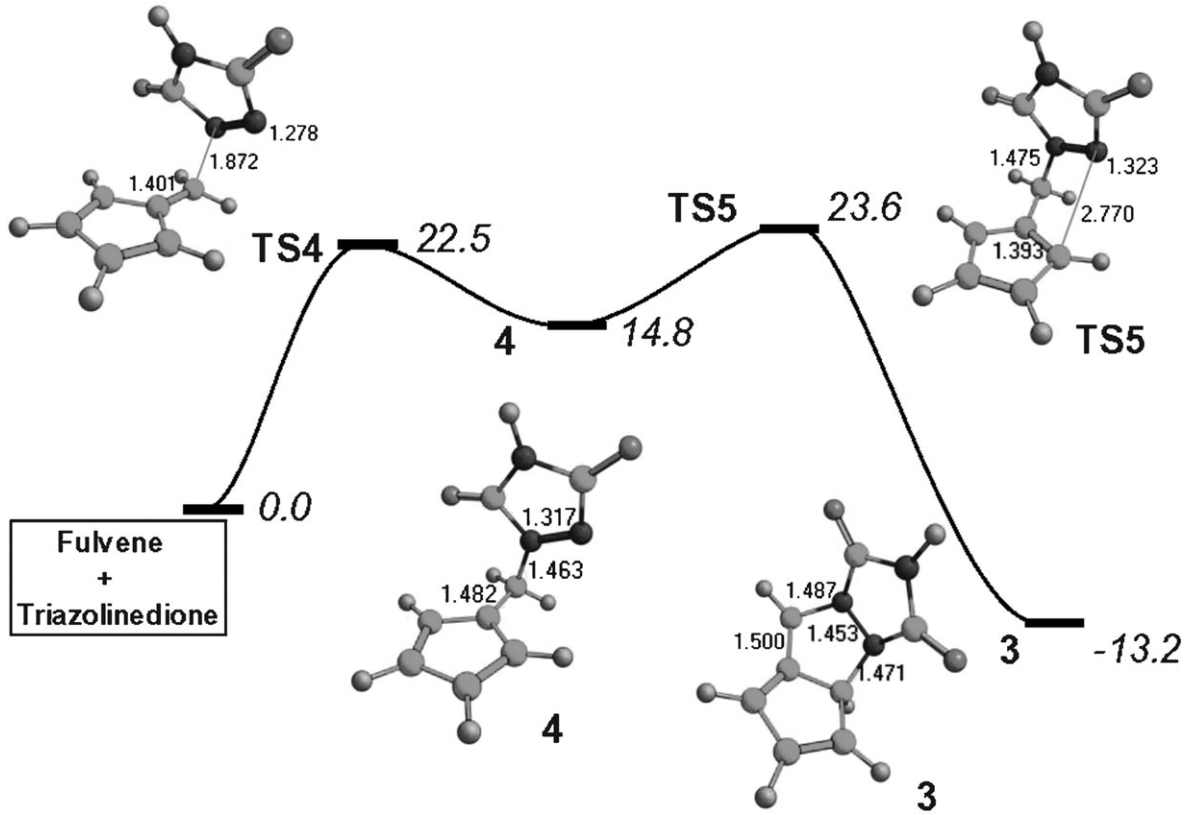


Fig. 7 Free energy profile for the nucleophilic reaction between pentafulvene and triazolinedione. Values in square brackets are the corresponding enthalpy change. Distances in Å and energies in kcal mol^{-1}.

were recorded under EI/HRMS (at 5000 resolution) using JEOL JMS 600H mass spectrometer. Abbreviations used in ^{1}H NMR are s = singlet, br s = broad singlet, d = doublet, dd = doublet of doublets, q = quartet and m = multiplet.

Theoretical calculations

All the molecular geometries were optimized at the DFT level by using the Becke's three-parameter exchange functional (B3)[14] in conjunction with the Lee–Yang–Parr correlation functional (LYP)[15] as implemented in the Gaussian 03 suite of programs.[16] For H, C and O, 6-31G(d) basis functions were selected.[17] Normal coordinate analysis has been performed for all stationary points to characterize the transition states and energy minimum structures. For most TSs, the analysis including the visualization of the negative frequency was sufficient to specify the corresponding reaction path. In some cases, intrinsic reaction coordinate (IRC) calculations near the TS region followed by geometry optimization of both reactants and products were performed to confirm the connectivity of the TSs.[18] Unscaled vibrational frequencies were used to calculate zero-point energy (ZPE) correction to the total energy. The Gibbs free energies were also calculated employing the usual approximations of statistical thermodynamics (ideal gas, harmonic oscillator, and rigid rotor) at the temperature of 298.15 K and pressure of 1.00 atm. Unless otherwise noted, the Gibbs free energy changes are used throughout in the text. Molecular electrostatic potential (MESP) was also calculated for selected systems at the B3LYP/6-31G(d) level. The MESP, a scalar property of a molecule is used here to explore the molecular reactivity.

The MESP of a molecule is a real physical property and can be determined experimentally by X-ray diffraction techniques or calculated rigorously from its electron density, $\rho(\boldsymbol{r})$, distribution by employing the equation.

$$V(\boldsymbol{r}) = \sum_{A}^{N} \frac{Z_A}{|\boldsymbol{r} - \boldsymbol{R}_A|} - \int \frac{\rho(\boldsymbol{r}')\mathrm{d}^3\boldsymbol{r}'}{|\boldsymbol{r} - \boldsymbol{r}'|} \qquad (1)$$

where Z_A is the charge on nucleus A, located at $\boldsymbol{R}_A$.[19] MESP is used widely for understanding molecular reactivity, intermolecular interactions, molecular recognition, electrophilic reactions and a variety of chemical phenomena.[20] Visualization of MESP is a good way to see the charge distribution within a molecule. Local minima of MESP (V_{min}) is often observed at the lone pair region of a molecule because of the larger value of the electronic term in eqn (1) as compared to the nuclear term and these V_{min} points represented centers of negative charge on the molecule.[19b] At these minima ∇V will be zero and the Hessian matrix of $V(\boldsymbol{r})$ will have three positive eigenvalues.

Syntheses

Typical procedure for 1a and 1b. To a solution of 4-phenyl-2,4,6-triazoline-3,5-dione **B** (100 mg, 0.58 mmol), in ethyl acetate (20 mL), at 0 °C, 6,6′-diphenylfulvene **A** (65 mg,

0.28 mmol) was added slowly under N_2 atmosphere. The reaction mixture was stirred for 2 h at room temperature. After monitoring the reaction by TLC, the reaction mixture was diluted with water (50 mL) and extracted using ethyl acetate (3 × 50 mL). The combined organic layers were washed with saturated brine solution and dried over anhydrous sodium sulfate. The crude product obtained was purified by silica gel column chromatography to afford the products **1a** (84 mg) and **1b** (72 mg) in 81% yield (1 : 1.2).

Data for **1a**. Colorless solid, mp 247 °C. R_f = 0.58 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3064, 2926, 2857, 1769, 1718, 1600, 1497, 1407, 1280, 1134, 913, 758, 700, 648, 505 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.53–7.14 (m, 30 H), 6.26 (dd, J_1 = 2.8 Hz, J_2 = 5.6 Hz, 1H), 5.87 (d, J = 5.8 Hz, 1H), 5.04 (d, J = 8.5 Hz, 1H), 4.36 (s, 1H), 4.13 (s, 2H), 3.94 (s, 1H), 3.65 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 152.9, 150.7, 150.2, 149.0, 140.6, 140.4, 138.4, 138.0, 134.2, 133.6, 131.3, 130.7, 130.5, 129.8, 129.3, 129.1, 129.0, 128.9, 128.8, 128.5, 128.4, 128.0, 127.9, 127.8, 127.1, 126.8, 125.4, 75.2, 64.0, 53.3, 46.3, 41.5, 30.3, 29.6, 14.0. MS (FAB, M + 1): calc. for $C_{52}H_{38}N_6O_4$: 811.30, found: 812.04.

Data for **1b**. Light yellow solid, mp 150 °C. R_f = 0.27 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3065, 2957, 2855, 1768, 1734, 1597, 1498, 1396, 1283, 1142, 1014, 916, 749, 696, 642, 508 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.55–7.16 (m, 20H), 7.03 (d, J = 5.6 Hz, 1H), 6.47–6.45 (m, 1H), 5.56 (s, 1H), 4.73 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 157.4, 155.7, 150.2, 149.4, 138.6, 136.5, 130.9, 130.4, 129.5, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 127.8, 127.7, 125.3, 125.2, 125.1, 123.6, 71.8, 62.1, 29.9, 29.3. MS (FAB, M + 1): calc. for $C_{34}H_{24}N_6O_4$: 581.19, found: 581.38.

Compound 2a and 2b. 81% Yield (2.4 : 1).

Data for **2a**. Yellow viscous liquid, mp 158 °C. R_f = 0.46 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3065, 2933, 2857, 1767, 1729, 1605, 1551, 1450, 1397, 1264, 1108, 1068, 1020, 844, 736, 711, 520 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.56–7.25 (m, 10H), 6.08 (s, 1H), 5.95–5.90 (m, 1H), 5.06–4.94 (m, 2H), 4.58 (s, 1H), 3.65 (m, 2H), 3.40 (s, 1H), 1.25 (m, 9H), 2.16–2.03 (m, 11H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 154.1, 153.8, 152.3, 136.5, 136.1, 135.8, 130.7, 128.8, 128.7, 128.6, 127.7, 127.1, 126.8, 125.6, 125.3, 75.6, 68.5, 65.4, 63.5, 60.1, 43.0, 42.3, 42.0, 40.3, 33.3, 32.2, 31.8, 30.1, 29.6, 25.3, 24.8, 23.3, 22.1. HRMS (EI, M^+): calc. for $C_{38}H_{38}N_6O_4$: 642.2955, found: 642.2975.

Data for **2b**. White solid, mp 190 °C. R_f = 0.21 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 2930, 2860, 1779, 1725, 1499, 1411, 1364, 1233, 1141, 1016, 795, 741, 644, 515 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.35 (m, 10H), 6.77 (d, J = 5.5 Hz, 1H), 6.46 (m, 1H), 5.52 (s, 1H), 4.21 (s, 1H), 2.17–1.50 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.6, 158.4, 154.0, 153.7, 133.1, 130.8, 129.3, 129.1, 128.9, 128.3, 125.7, 125.6, 72.6, 69.8, 61.8, 33.7, 32.0, 29.7, 29.1, 24.3, 14.2. MS (FAB, M + 1): calc. for $C_{27}H_{24}N_6O_4$: 497.19, found: 497.45.

Compound 3a and 3b. 62% Yield (1 : 2).

Data for **3a**. White solid, mp 198 °C. R_f = 0.51 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 2935, 1769, 1718, 1648, 1410, 1363, 1166, 947, 754, 753, 645 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.53–7.30 (m, 10 H), 6.07–6.01 (m, 1H), 5.95–5.91 (m, 1H), 5.31 (m, 1H), 4.57 (s, 1H), 4.52 (s, 2H), 4.25–4.15 (m, 1H), 3.40 (s, 1H), 2.30–0.88 (m, 24H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.9, 154.3, 153.8, 151.9, 135.6, 134.7, 133.8, 132.9, 131.1, 128.6, 128.4, 128.3, 127.8, 126.5, 126.1, 125.3, 125.0, 77.5, 73.3, 72.4, 64.5, 63.1, 62.1, 43.7, 43.1, 37.6, 36.5, 33.9, 33.1, 31.5, 30.4, 29.7, 24.4, 23.5. MS (FAB, M + 1): calc. for $C_{40}H_{42}N_6O_4$: 671.33, found; 671.61.

Data for **3b**. Light yellow solid, mp 174 °C. R_f = 0.23 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3051, 2924, 2857, 1784, 1721, 1595, 1498, 1406, 1279, 1235, 1142, 1017, 792, 739, 688, 640, 513 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.50–7.35 (m, 10H), 6.72 (d, J = 5.6 Hz, 1H), 6.43 (dd, J_1 = 2.2 Hz, J_2 = 5.6 Hz, 1H), 5.51 (s, 1H), 4.13 (s, 1H), 3.04–2.81 (m, 2H), 2.22–0.88 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 156.1, 153.1, 151.5, 133.1, 130.7, 129.3, 129.1, 128.8, 128.2, 125.6, 125.5, 116.8, 73.03, 72.6, 61.9, 51.3, 37.6, 34.4, 31.7, 30.5, 24.7, 23.6. MS (FAB, M + 1): calc. for $C_{28}H_{26}N_6O_4$: 511.20, found: 512.38.

Compound 4a and 4b. 86% Yield (1 : 2).

Data for **4a**. Brown viscous liquid. R_f = 0.36 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3024, 2402, 1777,1700, 1521, 1428, 1220, 1111, 929, 769, 478 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.39–7.25 (m, 10H), 6.02–5.97 (m, 2H), 5.60 (s, 1H), 4.66 (d, J = 7.6 Hz, 1H), 4.60 (s, 2H), 4.57 (s, 2H), 4.17–4.07 (m, 1H), 3.59–3.55 (m, 2H), 3.47–3.41 (m, 1H), 1.78–1.23 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 153.9, 153.0, 150.4, 136.5, 135.9, 135.8, 130.8, 128.7, 128.6, 128.5, 128.0, 127.8, 75.6, 73.8, 68.4, 65.5, 63.5, 60.5, 45.7, 43.4, 41.9, 34.8, 33.4, 31.7, 29.7, 29.3, 24.9, 24.8, 24.6, 24.1, 23.3, 14.1. MS (FAB, M + 1): calc. for $C_{40}H_{42}N_6O_4$ 671.33, found: 671.83.

Data for **4b**. Light brown viscous liquid. R_f = 0.21 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3037, 2933, 2856, 1760, 1717, 1441, 1406, 1378, 1155, 1071, 944, 739, 697 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34–7.16 (m, 10H), 6.44 (d, J = 5.6 Hz, 1H), 6.15 (dd, J_1 = 2.3 Hz, J_2 = 5.6 Hz, 1H), 5.30 (s, 1H), 4.58 (s, 2H), 4.47 (s, 2H), 3.97 (s, 1H), 2.57–2.53 (m, 2H), 1.76–1.24 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.7, 158.4, 154.0, 153.7, 135.5, 134.8, 132.8, 130.0, 128.8, 128.7, 128.6, 128.5, 128.3, 127.9, 92.1, 72.5, 69.5, 61.1, 43.8, 33.3, 32.3, 29.3, 24.7, 23.2, 22.7, 14.2. HRMS (EI^+): calc. for $C_{29}H_{28}N_6O_4$: 524.2172, found: 525.5527.

Compound 5b. 77% Yield, white solid, mp 142 °C. R_f = 0.24 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 2928, 1763, 1719, 1442, 1411, 1353, 1163, 945, 782, 751, 703, 640 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34–7.20 (m, 10H), 6.44 (d, J = 5.6 Hz, 1H), 6.16 (dd, J_1 = 2.1 Hz, J_2 = 5.6 Hz, 1H), 5.32 (s, 1H), 4.59 (s, 2H), 4.50 (s, 2H), 3.92 (s, 1H), 2.87–2.71 (m, 2H), 2.14–0.90 (m, 10 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.7, 158.1, 153.7, 152.6, 135.4, 134.8, 132.0, 130.1, 128.9, 128.6, 128.3, 128.1,

128.0, 127.9, 127.6, 114.9, 94.1, 73.4, 62.3, 44.0, 43.3, 37.1, 33.6, 31.6, 29.1, 25.2, 23.3. MS (FAB, M + 1): calc. for $C_{36}H_{30}N_6O_4$: 539.23, found: 539.36.

Compound 6a and 6b. 92% Yield (1 : 2).

Data for **6a**. Light yellow viscous liquid. R_f = 0.52 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 2925, 2854, 1767, 1712, 1494, 1435, 1352, 1216, 1121, 1069, 939, 752, 698, 540 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.34–7.00 (m, 30 H), 6.00 (dd, J_1 = 3.0 Hz, J_2 = 5.7 Hz, 1H), 5.69 (d, J = 5.7 Hz, 1H), 4.82 (d, J = 8.7 Hz, 1H), 4.53 (s, 2H), 4.48 (s, 2H), 4.12 (s, 1H), 4.00 (s, 1H), 3.91 (d, J = 6.6 Hz, 1H), 3.70 (s, 1H), 3.44–3.42 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.9, 152.9, 150.2, 149.9, 140.6, 138.4, 138.1, 134.3, 133.7, 131.4, 130.8, 130.6, 129.9, 129.7, 129.3, 129.2, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.8, 126.0, 125.5, 114.4, 93.1, 75.3, 57.8, 64.0, 53.4, 46.4, 38.7, 29.3, 22.9. MS (FAB, M + 1): calc. for $C_{54}H_{42}N_6O_4$: 839.33, found: 840.28.

Data for **6b**. Light brown viscous liquid. R_f = 0.26 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3065, 2926, 2857, 1957, 1771, 1730, 1612, 1492, 1408, 1352, 1279, 1159, 1074, 947, 904, 753, 703, 648 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.15 (m, 20H), 6.77 (d, J = 5.6 Hz, 1H), 6.13–6.10 (m, 1H), 5.32 (s, 1H), 4.56 (s, 2H), 4.46 (s, 1H), 4.36 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 157.4, 152.2, 151.6, 138.7, 136.9, 135.2, 134.9, 131.0, 130.8, 129.5, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.4, 127.3, 93.1, 72.4, 68.0, 62.0, 43.5, 38.7, 29.7, 28.9, 23.8, 22.7. MS (FAB, M + 1): calc. for $C_{36}H_{28}N_6O_4$: 609.23, found: 609.74.

Compound 7b. 78% Yield, light brown viscous liquid. R_f = 0.38 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3057, 2938, 2858, 1770, 1729, 1618, 1516, 1441, 1407, 1352, 1157, 927, 765, 701, 649 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.51–7.47 (m, 4H), 7.37–7.25 (m, 6H), 7.11–7.00 (m, 8H), 6.75 (d, J = 5.6 Hz, 1H), 6.10 (dd, J_1 = 2.3 Hz, J_2 = 5.7 Hz, 1H), 5.30 (s, 1H), 4.59–4.50 (m, 1H), 4.45 (s, 2H), 4.31 (s, 2H), 2.30 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.9, 157.5, 152.2, 151.5, 138.8, 137.7, 137.5, 137.0, 132.3, 132.1, 131.0, 129.5, 129.3, 129.2, 129.1, 129.0, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 92.4, 72.3, 62.2, 43.3, 43.0, 21.2, 14.3. MS (FAB, M + 1): calc. for $C_{38}H_{32}N_6O_4$: 637.26, found: 637.68

Compound 8a and 8b. 85% Yield (2.1 : 1).

Data for **8a**. White solid, mp 135 °C. R_f = 0.53 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 2939, 2861, 1759, 1702, 1517, 1439, 1413, 1353, 1140, 1099, 927, 766, 737, 649 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J = 8.4 Hz, 4H), 7.11 (d, J = 7.6 Hz, 4H), 6.03–5.96 (m, 2H), 5.60 (s, 1H), 4.66 (d, J = 8.4 Hz, 1H), 4.58–4.99 (m, 4H), 4.13 (d, J = 6.9 Hz, 1H), 3.57–3.54 (m, 2H), 3.46–3.39 (m, 1H), 2.26 (s, 6H), 2.22–1.25 (m, 20H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 153.0, 152.5, 150.2, 137.7, 137.6, 133, 132.9, 132.8, 130.8, 129.3, 128.7, 128.6, 127.8, 75.6, 73.7, 68.4, 65.5, 63.5, 60.4, 45.6, 42.8, 41.8, 34.8, 33.3, 31.7, 29.9, 24.9, 24.6, 24.0, 23.3, 21.1. MS (FAB, M + Na^+): calc. for $C_{42}H_{46}N_6O_4$: 698.36, found: 721.26.

Data for **8b**. Yellow solid, mp 142 °C. R_f = 0.38 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 2934, 2859, 1780, 1704, 1517, 1442, 1353, 1265, 1134, 928, 767, 736, 649 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.28 (d, J = 8.5 Hz, 4H), 7.10 (d, J = 8.1 Hz, 4H), 6.48 (d, J = 5.6 Hz, 1H), 6.18 (dd, J_1 = 2.2 Hz, J_2 = 5.6 Hz, 1H), 5.31 (s, 1H), 4.67 (d, J = 8.5 Hz, 1H), 4.58–4.52 (br s, 4H), 2.35 (s, 6H), 2.05–1.25 (m, 10H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.7, 154.4, 153.2, 152.7, 137.9, 136.6, 133.1, 132.6, 131.0, 130.3, 129.6, 129.5, 129.4, 128.8, 128.7, 128.6, 127.9, 92.3, 73.9, 68.6, 63.7, 43.0, 41.9, 32.6, 30.2, 25.9, 24.8, 23.6, 23.5, 21.3. MS (FAB, M + Na): calc. for $C_{31}H_{32}N_6O_4$, 552.25, found: 573.72.

Compound 9a and 9b. 61% Yield (1.7 : 1).

Data for **9a**. Light brown solid, mp 236 °C. R_f : 0.68 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 3060, 2933, 2856, 1760, 1705, 1494, 1448, 1416, 1381, 1220, 1164, 1002, 859, 757, 699, 656 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.40–7.10 (m, 20H), 6.10 (dd, J_1 = 3.0 Hz, J_2 = 5.8 Hz, 1H), 5.77 (d, J = 5.9 Hz, 1H), 4.88 (d, J = 8.4 Hz, 1H), 4.18 (s, 1H), 4.08 (s, 1H), 3.99 (d, J = 6.8 Hz, 1H), 3.77–3.67 (m, 3H), 3.54–3.48 (m, 1H), 2.03–2.00 (m, 4H), 1.79–1.58 (m, 8H), 1.28–1.20 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.8, 152.5, 151.22, 150.4, 140.8, 140.6, 138.4, 138.1, 134.4, 133.5, 131.3, 129.7, 129.1, 128.7, 128.2, 127.9, 127.8, 127.7, 127.4, 16.8, 77.2, 76.2, 75.3, 74.2, 63.8, 52.2, 46.4, 41.8, 29.5, 29.2, 28.9, 26.9, 25.7, 24.9. MS (FAB, M + 1): calc. for $C_{52}H_{50}N_6O_4$: 823.39, found: 823.57.

Data for **9b**. Light brown viscous liquid. R_f = 0.24 (1 : 1 hexane–ethyl acetate). IR (Neat) ν_{max}: 2937, 2858, 1778, 1724, 1496, 1410, 1364, 1237, 1145, 1011, 798, 646 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.48–7.25 (m, 10H), 6.70 (d, J = 5.6 Hz, 1H), 6.39 (m, 1H), 5.50 (s, 1H), 4.21 (s, 1H), 3.71–3.63 (m, 1H), 3.51–3.47 (m, 1H), 2.09–2.01 (m, 4H), 1.83–1.57 (m, 8H), 1.38–1.19 (m, 8H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3, 158.1, 154.0, 153.7, 133.1, 130.8, 129.3, 129.1, 128.9, 128.3, 125.7, 125.6, 72.6, 69.8, 61.8, 33.7, 32.0, 29.7, 29.1, 24.3, 14.2. MS (FAB, M + Na^+): calc. for $C_{34}H_{36}N_6O_4$: 592.28, found: 615.26.

Experimental procedure for 1c and 1d. To a solution of 6,6′-diphenylfulvene **A** (65 mg, 0.28 mmol) in 20 mL methanol at −40 °C, 4-phenyl-2,4,6-triazoline-3,5-dione **B** (50 mg, 0.28 mmol) in dichloromethane (4 mL) was added slowly under N_2 atmosphere. The reaction mixture was stirred at this temperature for 1 h and then slowly brought to r.t. and stirring continued for 1 h. After monitoring the reaction by TLC, the solvent was evaporated at reduced pressure. The crude product obtained was purified by silica gel column chromatography to afford the products **1c** (53 mg, 46%) and **1d** (24 mg, 21%) in 67% yield.

Data for **1c**. Viscous liquid. R_f = 0.35 (1 : 2 hexane–ethyl acetate). IR (Neat) ν_{max}: 2930, 1772, 1697, 1502, 1423, 1280, 1226, 1069, 758 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.30–7.08 (m, 16H), 6.66 (d, J = 6.1 Hz, 1H), 6.29 (dd, J_1 = 2.4 Hz, J_2 = 6.3 Hz, 1H), 5.78 (d, J = 6.3 Hz, 1H), 4.50 (dd, J_1 = 2.4 Hz, J_2 = 6.3 Hz, 1H), 3.41 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 153.3, 150.4, 141.9, 140.3, 138.3, 135.6, 133.1, 131.6, 130.2, 129.3, 128.8, 128.4, 128.3, 1227.9,

127.7, 125.4, 113.4, 57.8, 56.2, 29.7. MS (FAB, M + Na^+): calc. for $C_{27}H_{23}N_3O_3$: 437.17 found: 460.23.

Data for **1d**. White solid, mp 148 °C. R_f = 0.29 (1 : 2 hexane–ethyl acetate). IR (Neat) ν_{max}: 2929, 2854, 17702, 1695, 1500, 1428, 1277, 1222, 1121, 1069, 760, 645 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.30–7.08 (m, 16H), 6.50 (d, J = 6.0 Hz, 1H), 6.17 (dd, J_1 = 2.4 Hz, J_2 = 6.0 Hz, 1H), 5.71 (s, 1H), 4.55 (d, J = 2.4 Hz, 1H), 3.33 (s, 3H). NMR (75 MHz, $CDCl_3$): δ 153.4, 151.0, 145.3, 141.4, 140.7, 137.6, 135.8, 134.0, 131.9, 130.9, 129.2, 129.0, 128.6, 128.5, 128.1, 127.5, 127.1, 125.8, 113.1, 57.7, 56.2, 27.3. MS (FAB, M + Na^+): calc. for $C_{27}H_{23}N_3O_3$: 437.17, found: 460.50.

X-Ray crystallography

The single-crystal diffraction data were collected on a Bruker AXS Smart Apex CCD diffractometer at 100(2) K. The X-ray generator was operated at 50 kV and 30 mA using Mo-Kα radiation. The data was reduced using SAINTPLUS and an empirical absorption correction was applied using the package SADABS. XPREP was used to determine the space group. The crystal structure was solved by direct methods using SHELXS97 and refined by full-matrix least squares methods using SHELXL97. Molecular and packing diagrams were generated using ORTEP-III and PLATON. All the hydrogen atoms of the compound were set in calculated positions and refined as riding atoms.

Crystal data for 1a. $C_{52}H_{38}N_6O_4 \cdot C_4H_8O_2$, M_r = 898.99; crystal size: 0.20 × 0.16 × 0.08 mm; triclinic, space group $P\bar{1}$; a = 12.2707(13), b = 13.5989(15), c = 15.4906(17) Å, α = 71.100(2), β = 73.300(2), γ = 72.169(2)°, Z = 2, V = 2276.7(4) $Å^3$, D_c = 1.311 g cm^{-3}; λ = 0.71073 Å; μ = 0.087 mm^{-1}, θ_{max} = 28.26°; no. of reflections collected = 13 579; no. of independent reflections = 9964; no. of parameters = 612; R_{int} = 0.0285; $F(000)$ = 944; T = 100 K; GOF on F^2 = 1.025; $R1/wR2$ ($[I > 2\sigma(I)]$ = 0.0738/0.1924; $R1/wR2$ (all data) = 0.1444/0.2350. CCDC reference number 275653. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b614533g

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