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Computational and Experimental Studies on the Hetero-Diels-Alder Reactions of Cross-conjugated Enaminones with Sulphene

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ABSTRACT

***Ab initio* and density functional theory (DFT) calculations have been used to investigate the feasibility of cycloaddition reactions of enaminones 1 with sulphene. Specifically, the geometry optimizations, frequency calculations and self-consistent reaction-field (SCRF) solvent simulations in combination with higher-quality relative energies carried out at the DFT level using the 6-31+G(d) basis set suggests that the product obtained is both thermodynamically and kinetically preferred, indicating the feasibility of this reaction. Additionally, experimental studies carried out on the reactions of these enaminones 1 with sulphene were also found to be in agreement with the theoretical predictions resulting in the synthesis of a variety of novel oxathiine derivatives having great biological and medicinal importance.**

KEYWORDS

Enaminones, cycloadditions, sulphene, DFT, SCRF.

1. Introduction

One of the most widely used reactions in multiple step synthesis[1] of natural products and heterocyclic compounds is the Diels-Alder (DA) reaction.[2] This reaction is of great value in organic synthesis and is a key step in the construction of compounds containing six-membered rings.[3] A number of reports showing the utilization of a variety of heterodienes in cycloaddition reactions leading to the synthesis of various heterocyclic compounds have been documented in the literature.[4] Recently, diene-transmissive hetero-Diels-Alder (DTHDA) reactions emerged as an efficient methodology for the construction of ring fused heterobicycles by carrying out multi-domino cycloaddition reactions of cross-conjugated precursors in a stereo-controlled manner.[5] This approach is not restricted to intermolecular-intermolecular cycloadditions but also employs intramolecular-intermolecular and intramolecular-intramolecular modes of diene transmissive hetero-Diels Alder reactions.[6] Tsuge and coworkers have reported the reactions of various carbotrienes with some reactive diazodienophiles[5e] and of divinylketones with enamines as the first cycloaddition followed by the second cycloaddition with strong dienophiles such as tetracyanoethylene and triazoline-dione,[5f] utilizing the diene-transmissive Diels-Alder approach. Motoki *et al.* reported the utilization of divinyl thioketones[5a] as heterotrienes in diene-transmissive hetero-Diels-Alder reactions. The reported intramolecular-intermolecular and intramolecular-intramolecular modes of diene-transmissive hetero-Diels-Alder cycloadditions of divinylthioketones were found to be quite useful for the synthesis of fused heterocycles[5b] with high efficiency and predictable diastereoselectivity.

A literature survey reveals that although the DA cycloaddition reactions of simple enaminoketones with some dienophiles have been reported,[7] the cross-conjugated dienones **1** have been much less explored in organic synthesis under DA reaction conditions, despite possessing immense synthetic value. For example, the only reported [4+2] cycloaddition reaction of enaminones of type **1** involves their reaction with dichloroketene, yielding pyranone derivatives.[8] It has also been reported[8] that, despite the high reactivity of sulphenes as dienophiles, they fail to react with open chain enaminoketones **1** lacking substituents at the C-2 position (Scheme 1).

Subsequently, theoretical studies have been performed to gain a better understanding of the feasibility of the reaction between **1** and sulphene, indicating equal probability for the formation of both products (**2** and **3**) under experimental conditions. For this purpose, *ab initio* and DFT calculations have been performed to explore the energetics of all reactants (**1** and sulphene) and the corresponding cycloadducts (**2** and **3**) with dimethylamine (DMA) (Scheme 1). The broader goal of this work was to assess the feasibility of this reaction both in the gas phase as well as in solution. This paper is divided into two sections; the first section comprises a theoretical study to assess the feasibility of the reaction (Scheme 1), carried out both in the gas phase as well as in solution using dichloromethane (DCM), followed by the experimental section providing details for the synthetic route of this reaction. The selection of dichloromethane as a solvent for these theoretical calculations was made on the basis of its preference over other solvents for similar types of cycloadditions under experimental conditions, as reported in the literature.[4a–e]

2. Computational Methodology

2.1. Gas Phase Calculations

All the reactants and products shown in Scheme 1 were drawn using the Visualizer module of Materials Studio (MS) ver. 4.1,[9] and were geometrically optimized at the ab initio SCF level using the 6-31+G(d) basis set, and the Gaussian 03 computer program.[10]

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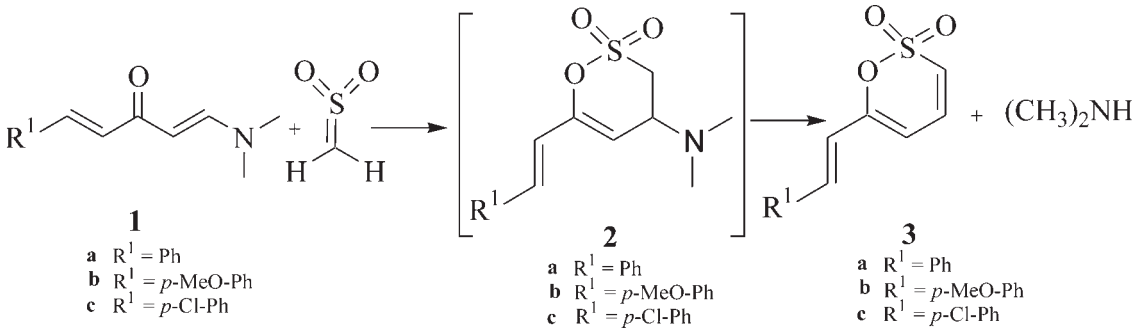


Scheme 1

Density functional theory (DFT) offers a promising tool with inclusion of some electron correlation that may be applied to large systems due to its computational efficiency compared with the MP2 level and above. Frequency analyses were also carried out to verify the nature of all the stationary points obtained and to calculate the zero-point vibrational energies (ZPVE) and both thermal and entropic corrections. Consequently DFT calculations were performed using Becke's three-parameter hybrid functional (B3) with the Lee, Yang and Parr (LYP) expression for the non-local correlation (B3LYP).[11] All calculations presented in this work were compared with the performance of the DFT calculations using the B3LYP method combined with the 6-31+G(d) basis set. In order to evaluate the effect of electron correlation, single-point MP2/6-31+G(d) calculations were also performed on all structures shown in Scheme 1 using the geometries obtained from the B3LYP-level geometry optimizations. These statistical terms were used to compute the thermodynamic properties including the enthalpy (ΔH) and the Gibbs energy (ΔG) of reaction in the gas phase at the B3LYP/6-31+G (d) level, according to Eqs. 1 and 2, respectively.

$$\Delta H = H_{product} - H_{reactant} \quad (1)$$

$$\Delta G = G_{product} - G_{reactant} \quad (2)$$

2.2. Self-consistent Reaction-field (SCRF) Calculations

To obtain an estimation of the solvation effects on the relative feasibilities of the reactions outlined in Scheme 1, single-point energy calculations were also carried out on the B3LYP/6-31+G(d) optimized structures using the self-consistent reaction-field (SCRF) model. In general, the SCRF methods treat the solute at the quantum mechanical level, while the solvent is represented as a dielectric continuum. In the description of the solvent, we chose the Polarizable Continuum Model (PCM) developed by Tomasi and coworkers.[12] Specifically, the PCM calculations were performed at the DFT level using B3LYP/6-31+G(d) and the standard protocol with the relative permittivity of dichloromethane (DCM) set to 8.93. The method calculates the size of the cavity created by the molecule in the solvent by default by using a series of overlapping spheres for the atoms. It should be noted that the SCRF Gibbs energy of solvation (ΔG_{sol}) reported in Table 3B was computed by single-point energies as the addition of three contributions: cavitation (ΔG_{cav}), van der Waals term (ΔG_{vw}) and electrostatic (ΔG_{ele}) Gibbs energies according to Eq. 3:

$$\Delta G_{sol} = \Delta G_{cav} + \Delta G_{vw} + \Delta G_{ele} \quad (3)$$

3. Computational Results and Discussion

3.1. Gas Phase Results

All structures were optimized and characterized by frequency analysis as energy minima. The optimized geometries of the products in the gas phase are displayed in Fig. 1. All the structures (**2a–c, 3a–c**) are true ground state minima, verified by second derivative calculations. A closer inspection of the optimized structures in Fig. 1 reveals that the phenyl group in (**2a**) is shifted by an angle of 45 ° closer to the -SO_2 group, in contrast to the linear position of the corresponding phenyl ring observed in (**3a**). This result is significant and the relative energies of the structures presented in Table 1 confirm that the cycloadduct (**2a**) is energetically more favoured than the corresponding cycloadduct (**3a**) at the DFT level. However, in the case of the geometries (**2b**) and (**3b**) no significant differences were observed. Interestingly (**3c**) is more folded or bent than (**2c**), but the latter is energetically more favoured than (**3c**). The relative energies of the reactants and products shown in Table 1 reveal a notable similarity between the different methods used for the calculations. In general, it should be noted that B3LYP calculations lead to a lower energy, which is even lower than those computed by the MP2 calculations. A closer inspection of Table 1a (see Supplementary Material online) points to the variation in ener-

Table 1 Relative energies of reactants and products in the gas phase [a].

Reaction	Compound/s	ΔE in gas phase/kJ mol^{-1}		
		HF/6-31+G(d)// HF/6-31+G(d)	B3LYP/6-31+G(d)// B3LYP/6-31+G(d)	MP2/6-31+G(d)// B3LYP/6-31+G(d)
1	1a + sulphene (r)	0	0	0
	2a (p)	–107.74	–120.33	–160.96
	3a + DMA (p)	–77.15	–45.69	–80.42
2	1b + sulphene (r)	0	0	0
	2b (p)	–142.05	–97.91	–176.06
	3b + DMA (p)	–101.96	–66.69	–99.79
3	1c + sulphene (r)	0	0	0
	2c (p)	–141.92	–90.33	–176.23
	3c + DMA (p)	–74.02	–35.52	–90.37

[a] Relative energies with respect to the reactants; (r) = reactant, (p) = product.

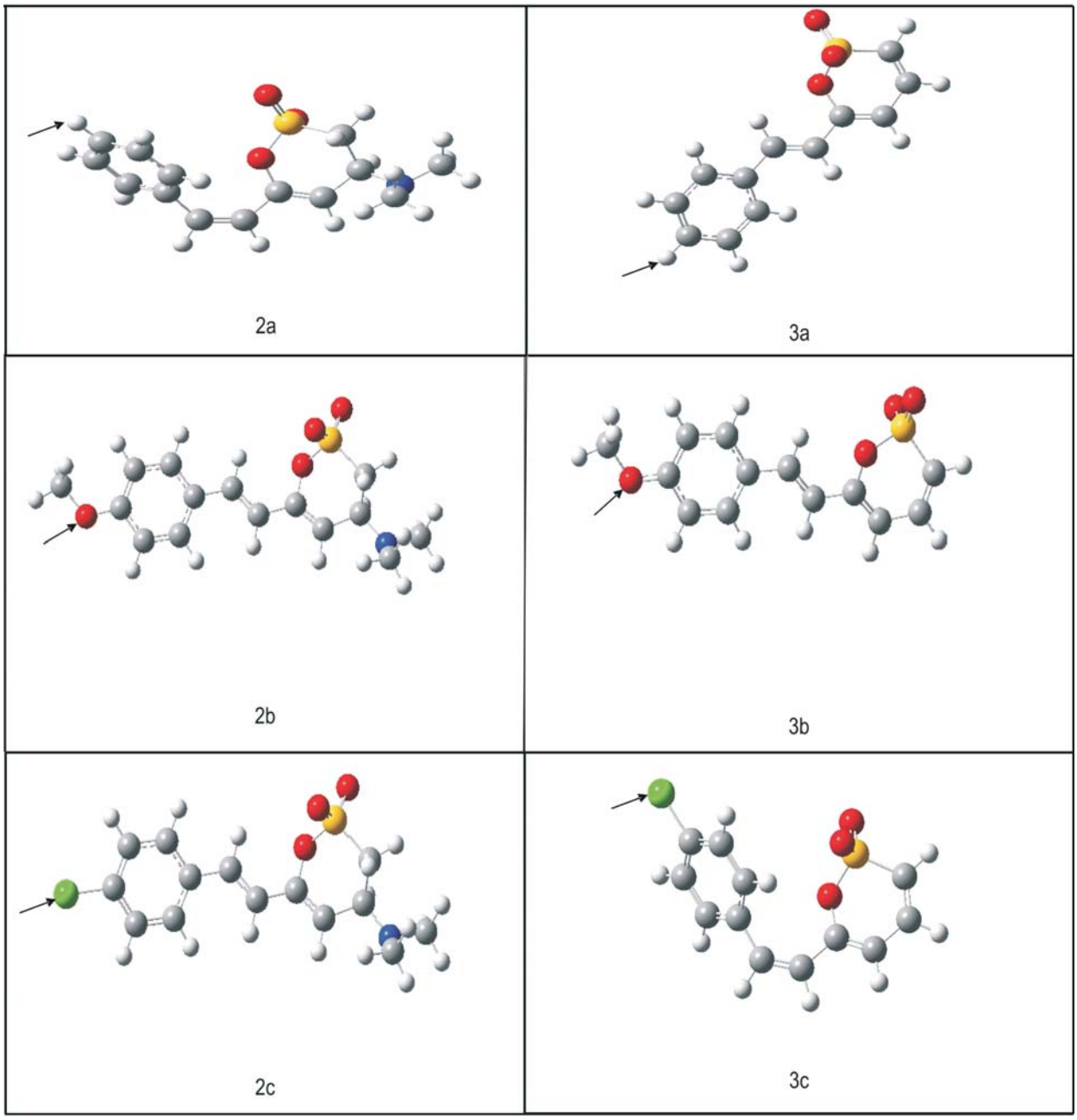


Figure 1 Energy-minimized structures of products 2 and 3 obtained at the B3LYP/6-31+G(d) level (in the gas phase); positions of substituents are indicated by arrows.

gies when the *para* hydrogen of the phenyl group in (**1, 2** and **3**) is replaced by either electron-donating (-OCH_3) or electron-withdrawing (-Cl) groups, with the electron-withdrawing group being energetically more favoured than the corresponding electron-donating groups. These findings are further supported by the relative energies with respect to the reactants (**1a–c**) + sulphene displayed in Table 1. The products (**2a–c**) are energetically more favoured than the corresponding products (**3a–c**) at all theoretical levels.

3.2. SCRF Results

The SCRF optimized geometries of the products in DCM are displayed in Fig. 2. The comparison of Figs. 1 and 2 indicates that the geometrical preferences of the methoxy and chloro groups are similar for both the gas phase and in DCM with no significant difference in the geometrical parameters observed. This is further confirmed by the total SCRF energies (see Table 2a in the Supplementary Material) along with the relative energies for the products **2** and **3** (Scheme 1) listed in Table 2. The SCRF energies are slightly lower than the corresponding gas phase energies shown in Table 1a (Supplementary Material), suggesting that the DCM environment does not introduce drastic changes to the overall energies of any of the individual compounds shown in Scheme 1. However, a closer inspection of the SCRF relative energies (Table 2) shows a difference in the results obtained with the corresponding gas phase relative energies shown in Table 1. From a qualitative point of view, both methods reflect that the products (**2a–c**) are energetically more favoured than the corresponding products (**3a–c**). However, a quantitative comparison of the ΔE values computed at the DFT level reveals that the gas phase results are systematically lower than those obtained using the SCRF method, with a difference of values ranging from 15.44 to 92.45 kJ mol^{-1}. This confirms that the overall products (**2a–c**) and (**3a–c**) in both the gas phase and SCRF medium are

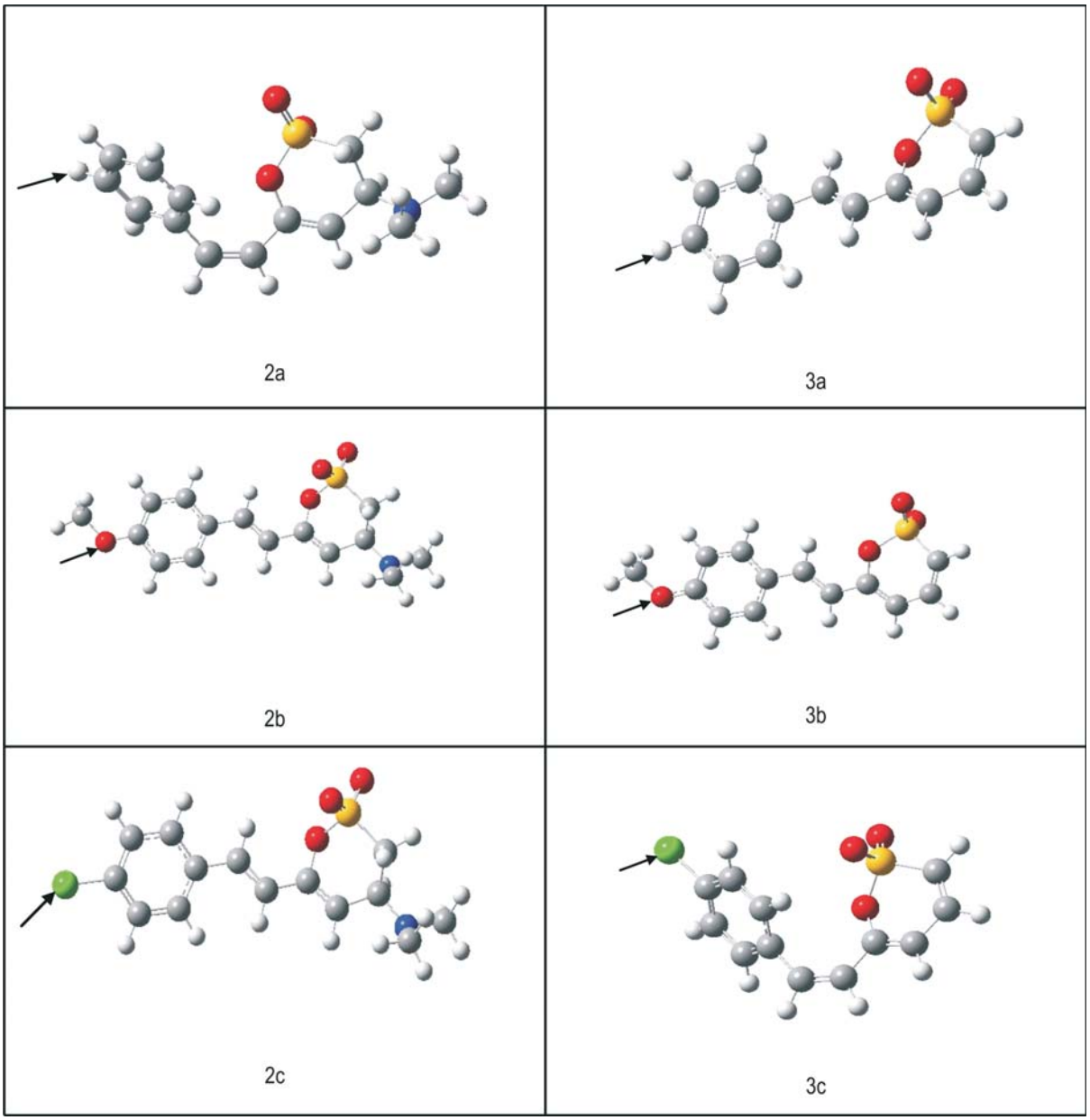


Figure 2 Energy-minimized structures of products 2 and 3 obtained at the B3LYP/6-31+G(d) level (in DCM); positions of substituents are indicated by arrows.

indeed sensitive to the geometry. Similar trends were observed at the HF and MP2 levels with the difference between SCRF and gas phase values ranging from 1.88 to 21.97 kJ mol^{-1}.

3.3 Thermochemical Results

The SCRF calculations yielded larger Gibbs energies of solvation (Table 3A, B) than the corresponding gas phase Gibbs energies, which range typically between –20.93 and –54.42 kJ mol^{-1} in the gas phase, and between –37.68 and –87.92 kJ mol^{-1} in dichloromethane (DCM). These results also confirm the preference of the formation of products (**2a–c**) over (**3a–c**), which is in accordance with our experimental findings mentioned in the synthesis section 4. It is worth mentioning that all the reactions are highly exothermic, confirming the feasibility of these reactions.

4. Synthesis Section

Following the theoretical section, the cycloaddition reactions of cross-conjugated enaminones **1** with sulphene were re-investigated. Interestingly, the enaminones **1** (1.0 eq) prepared according to the reported procedure,[13] after reaction with sulphene, generated *in situ* from methane sulphonyl chloride (1.1 eq) in the presence of triethylamine (1.2 eq) in dry dichloromethane (10 mL) at 0 °C, resulted in formation of compounds **2a–c**, in excellent yields (85–91 %) (Scheme 2, Table 4).

However, the same reaction, when examined in the presence of 3.0 eq of triethylamine, led to the isolation of products **3a–c** (72–82 %), formed *via* elimination of $(CH_3)_2NH$ from **2** in the presence of excess base. The conversion of **2** to **3** was also accomplished by refluxing of **2** in toluene for 27–28 h (Scheme 2).

The compounds **2** and **3** were characterized on the basis of analyzed data and spectral evidence. The compound 2,2-dioxo-6-styryl-3,4-dihydro-2λ^6-[1,2]oxathiin-4-yl)-dimethylamine (**2a**), for example, analyzed for $C_{14}H_{17}NO_3S$ and showed two characteristic SO_2 stretching absorptions around 1158 and 1373 cm^{-1} in its IR spectrum and exhibited a molecular ion peak at m/z 279 (M^+) in its mass spectrum. The presence of a singlet at δ 2.35 ppm (6H) for $-N(CH_3)_2$ protons, a dd (J = 11.4 and 13.2 Hz) at δ 3.24 ppm (1H) for a methylene proton, a ddd (J = 1.1, 6.3 and

Table 2 Relative energies of reactants and products in DCM [a].

Reaction	Compound/s	SCRF ΔE in DCM /kJ mol^{-1}		
		HF/6-31+G(d)// HF/6-31+G(d)	B3LYP/6-31+G(d)// B3LYP/6-31+G(d)	MP2/6-31+G(d)// B3LYP/6-31+G(d)
1	1A+sulphene (r)	0	0	0
	2a (p)	–84.64	–27.87	–139.75
	3a+DMA (p)	–73.35	–25.06	–77.57
2	1b+sulphene (r)	0	0	0
	2b (p)	–130.88	–71.09	–164.81
	3b+DMA (p)	–106.27	–53.01	–103.47
3	1c+sulphene (r)	0	0	0
	2c (p)	–132.34	–71.00	–166.19
	3c+DMA (p)	–75.90	–20.08	–92.63

[a] Relative energies with respect to the reactants; (r) = reactant, (p) = product.

13.2 Hz) at δ 3.50 ppm (1H) for another methylene proton, a ddd (J = 2.5, 6.3 and 11.4 Hz) at δ 4.11 ppm for –CH, a dd (J = 1.1 and 2.5 Hz) at δ 5.35 ppm for H_c, a doublet (J = 15.6 Hz) at δ 6.48 ppm for a *trans* olefinic proton (H_a) and a doublet (J = 15.6 Hz) at δ 6.99 ppm for another *trans* olefinic proton H_b, along with multiplets at δ 7.26–7.44 ppm corresponding to aromatic region protons, in its ^{1}H spectrum, confirmed the assigned structure. Further, the spectral peaks in its ^{13}C spectrum were also in agreement with the assigned structure.

Similarly, the compound **3a**, in its ^{1}H spectrum exhibited a doublet (J = 6.9 Hz) at δ 5.93 ppm for H_c, a doublet (J = 10.5 Hz) at δ 6.60 ppm for H_e, a doublet (J = 15.6 Hz) at δ 6.62 ppm for *trans* H_a, a dd (J = 6.9 and 10.5 Hz) at δ 6.85 ppm for H_d and a multiplet at δ 7.29–7.49 ppm corresponding to five aromatic protons along with the merged proton H_b. The structure of the compound **3a** was further corroborated by its ^{13}C spectrum. The molecular ion peak at m/z 234 (M^+) in its mass spectrum also confirmed the assigned structure.

In order to extend their synthetic versatility, a convenient methodology was developed for the transformation of **1** to **5** by treatment with aromatic amines **4** in refluxing toluene for 8–10 h (Scheme 3). A simple and convenient route for the synthesis of **5** is considered to be of great value since the earlier reported methods for the synthesis of **5** suffer from disadvantages such as multiplicity of steps and cumbersome procedures.[14] The treatment of **5a–c** with sulphene **6** led to the formation of cycloadducts **7a–c** in good yields (79–88 %, Table 4), which were also transformed to **3a** either by stirring in the presence of triethylamine or by refluxing in toluene (Scheme 3).

5. Conclusions

In this work we investigated the cycloaddition reaction of cross-conjugated enaminone **1** with sulphene, both in the gas phase and in solution in DCM, carried out at different computational levels. The computational results carried out at all three levels of theory support the formation of the products (**2a–c**) over (**3a–c**), in contrast to the experimental work reported[8] elsewhere in this paper, emphasizing the unreactive behaviour of enaminones towards sulphene. The results of the present work indicate that the geometrical preferences of (**2a–c**) and (**3a–c**) are similar in both the gas phase and in solution in DCM. Following these calculations, hetero-Diels-Alder reactions of

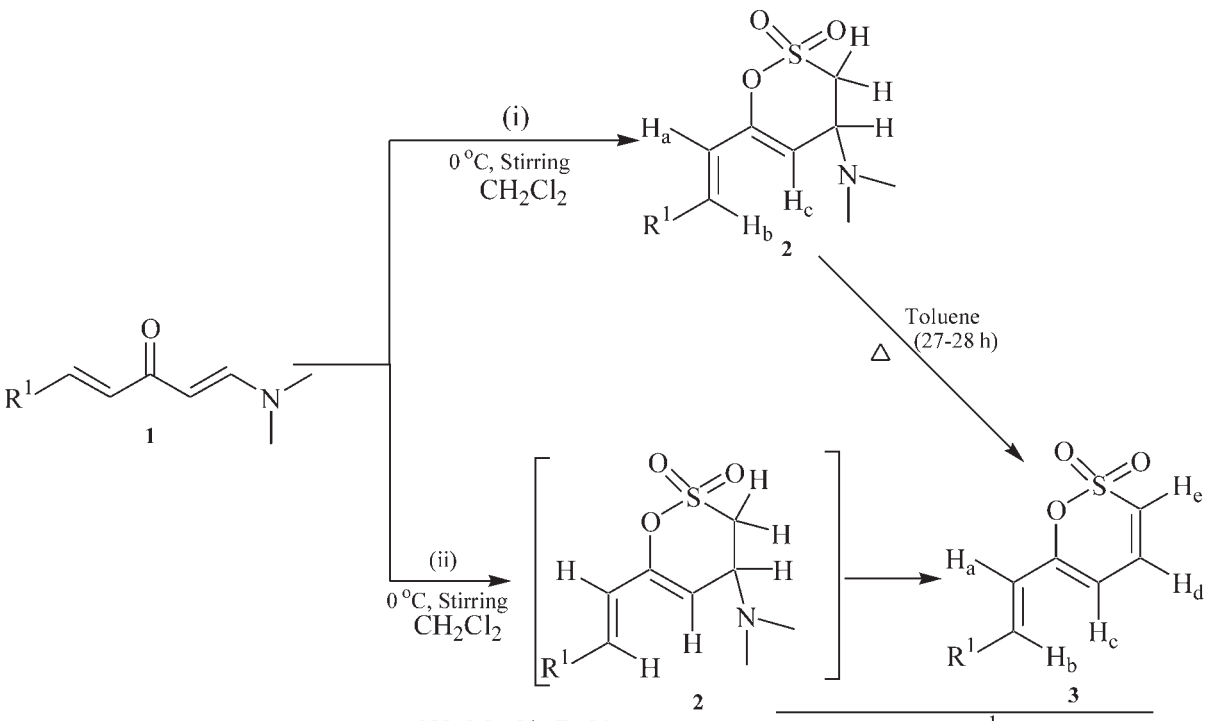
Table 3 (**A**) Thermochemical data of thermal enthalpies and thermal Gibbs energies computed in the gas phase; (**B**) SCRF Gibbs energy of solvation in DCM at the DFT level.

(A)	B3LYP/6-31+G(d) in the gas phase		
Reactant	Product	ΔH [a]/kJ mol^{-1}	ΔG [b]/kJ mol^{-1}
1a + sulphene ⟶	2a	–53.01	–15.73
1a + sulphene ⟶	3a + DMA	–45.15	–32.68
1b + sulphene ⟶	2b	–86.53	–22.51
1b+ sulphene ⟶	3b + DMA	–65.73	–54.10
1c + sulphene ⟶	2c	–85.56	–20.71
1c+ sulphene ⟶	3c + DMA	–35.82	–22.47

[a] $\Delta H = H_{product} - H_{reactant}$, [b] $\Delta G = G_{product} - G_{reactant}$

(B)		
Reactant	Product	ΔG_{sol} [a]/kJ mol^{-1}
1a + sulphene ⟶	2a	–46.28
1a + sulphene ⟶	3a + DMA	–46.61
1b + sulphene ⟶	2b	–90.25
1b+ sulphene ⟶	3b + DMA	–72.76
1c + sulphene ⟶	2c	–90.67
1c+ sulphene ⟶	3c + DMA	–38.28

[a] $\Delta G_{sol} = G_{product} - G_{reactant}$



Compound	R^1
1a	Ph
1b	*p*-CH_3O-Ph
1c	*p*-Cl-Ph
2a	Ph
2b	*p*-CH_3O-Ph
2c	*p*-Cl-Ph
3a	Ph
3b	*p*-CH_3O-Ph
3c	*p*-Cl-Ph

Scheme 2

cross-conjugated dienones **1** and **5** with sulphene have been successfully revisited, resulting in the synthesis of a series of novel oxathiine dioxide (**2**, **3** and **7**) derivatives possessing great medicinal and pharmacological importance. Our work has also demonstrated an easy route for the synthesis of N-aryl-substituted enaminones **5**.

6. Experimental

6.1. General

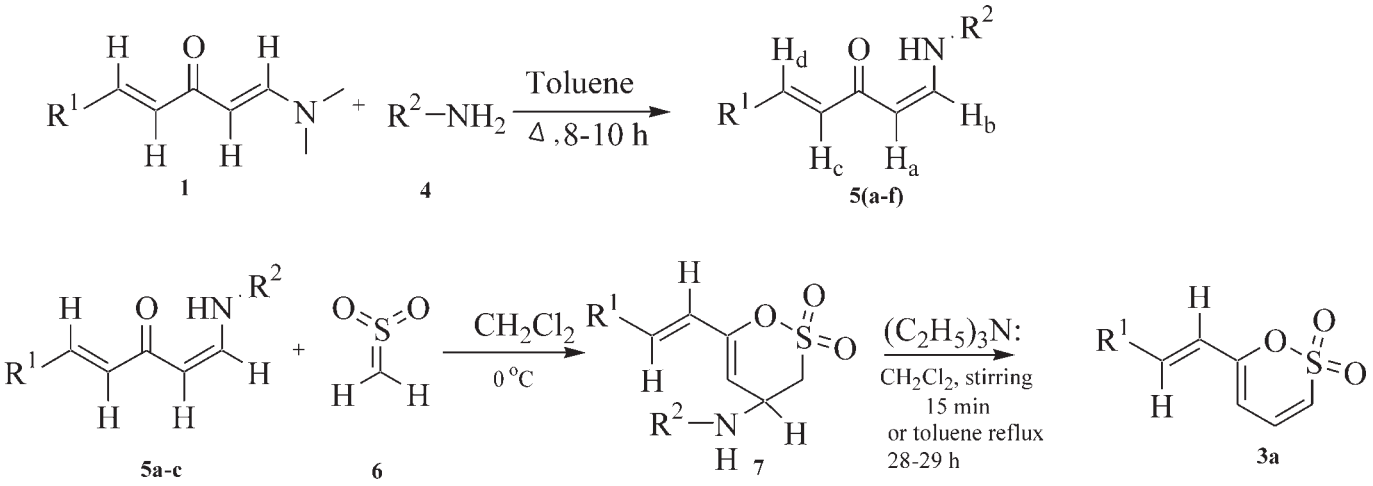
Melting points were determined by open capillary method using Veego Precision Digital Melting Point apparatus (Mumbai, India) and are uncorrected. IR spectra were recorded on a Shimadzu (Shanghai, China) D-8001 spectrophotometer. ^{1}H NMR spectra were recorded in deuterochloroform using Bruker (Geldermalsen, Netherlands) AC-E 200 (200 MHz) and AC-E 300 (300 MHz) spectrometers, using TMS as an internal standard. Chemical shift values are expressed as ppm downfield from TMS and J values are in Hz. Splitting patterns are indicated as s: singlet, d: doublet, dd: doublet of doublets, t: triplet, m: multiplet and q: quartet, bs: broad singlet. ^{13}C NMR spectra were also recorded on Bruker AC-E 200 (50.4 MHz) or AC-E 300 (75.0 MHz) spectrometers in deuterochloroform using TMS as an internal standard. Mass spectra were recorded on a Shimadzu (Shanghai, China) GCMS-QP-2000 mass spectrometer. Elemental analyses were performed on a Heraeus CHN-O-Rapid Elemental Analyzer (Hanau, Germany). Column chromatography was performed on a silica gel (60–120) mesh or Harrison Research Chromatotron (Palo Alto, CA, USA) using 2 mm plates (silica gel PF_{254}). Dichloromethane was dried over phosphorus pentoxide and stored over molecular sieves (4Å). DMF-DMA[15] and cross-conjugated enaminones[13] **1** were prepared according to the reported procedures. Methane sulphonyl chloride was distilled before use.

6.2. General Procedure for the Reaction of Enaminones 1 and 5 with Sulphene

To a well-stirred solution of enaminones **1** or **5** (10 mmol) and triethylamine (12 mmol (for **2** and **7**) and 30 mmol (for **3**)) in dry dichloromethane (30 mL) was added dropwise a solution of methane sulphonyl chloride in dry dichloromethane (30 mL) over a period of 30 min at 0 °C. After completion of the reaction (TLC), the reaction mixture was first washed with saturated sodium bicarbonate solution (2 × 25 mL) and water (2 × 50 mL) and the organic layer dried over anhydrous sodium sulphate. Removal of solvent under reduced pressure yielded the crude product, which was purified by silica gel column chromatography using a mixture of ethyl acetate and hexane (1:10, v/v).

6.3. General Procedure for the Conversion of 2 or 7 to 3

A solution of **2** or **7** (10 mmol) in dichloromethane (10 mL) was stirred with triethylamine (15 mmol) for 30 min. After completion (TLC), the reaction mixture was washed with saturated sodium



Compound	R^1	R^2
5a	Ph	Ph
5b	Ph	*p*-CH_3O-Ph
5c	Ph	*p*-tolyl
5d	*p*-MeO-Ph	Ph
5e	*p*-MeO-Ph	*p*-CH_3O-Ph
5f	*p*-MeO-Ph	*p*-tolyl
7a	Ph	Ph
7b	Ph	*p*-CH_3O-Ph
7c	Ph	*p*-tolyl
3a	Ph	-

Scheme 3

bicarbonate solution (2 × 25 mL) and extracted using dichloromethane. The crude product, obtained after removal of solvent under reduced pressure, was purified through silica gel column chromatography. The solid compounds **3** thus obtained were recrystallized using a chloroform and hexane (1:5, v/v) mixture.

Refluxing **2** or **7** in toluene for 27–28 h and purification through silica gel column chromatography of the crude reaction mixture accomplished another route for **3**. However, yield loss was observed in this case due to decomposition of the starting material.

From reaction of **1a** with sulphene (2,2-dioxo-6-styryl-3,4-dihydro-2H-2λ^6-[1,2]oxathiin-4-yl)-dimethyl amine **2a** (91 %) was obtained as a colourless crystalline solid; δ_H (300 MHz, $CDCl_3$): 2.35 [s, 6H, -N(CH_3)$_2$], 3.24 (dd, J 11.4 and 13.2 Hz, 1H, -CH_2), 3.50 (ddd, J 1.1, 6.3 and 13.2 Hz, 1H, -CH_2), 4.11 (ddd, J 2.7, 6.3 and 11.4 Hz, 1H, -CH), 5.35 (dd, J 1.1 and 2.4 Hz, 1H, H_c), 6.48 (d, J 15.6 Hz, 1H, H_a), 6.99 (d, J 15.6 Hz, 1H, H_b) and 7.26–7.44 ppm (m, 5H, ArH); δ_C (75 MHz, $CDCl_3$): 40.5 [N(CH_3)$_2$, 42.9 (-CH_2), 59.3 (-CH), 108.6, 119.6, 126.9, 128.6, 128.7, 131.4, 135.4 and 149.5 ppm; ν_{max} ($CHCl_3$): 1640, 1373 and 1158 cm^{-1}; m/z: 279 (M^+) (found: C, 60.26; H, 6.15, N, 5.06 %. calc. for $C_{14}H_{17}NO_3S$ (279); C, 60.19; H, 6.13, N, 5.01 %).

From reaction of **1b** with sulphene 6-[2-(4-methoxy-phenyl)-vinyl]-2,2-dioxo-3,4-dihydro-2H-2λ^6-[1,2]oxathiin-4-yl}-dimethyl amine **2b** (88 %) was obtained as a colourless solid; δ_H (300 MHz, $CDCl_3$): 2.34 [s, 6H, -N(CH_3)$_2$], 3.25 (dd, J 11.4 and 13.2 Hz, 1H, -CH_2), 3.52 (ddd, J 1.2, 6.3 and 13.2 Hz, 1H, -CH_2), 3.84 (s, 3H, -OCH_3), 4.11 (ddd, J 2.6, 6.5 and 11.4 Hz, 1H, -CH), 5.36 (d, J 2.5 Hz, 1H, H_c), 6.46 (d, J 15.6 Hz, 1H, H_a), 6.98 (d, J 15.6 Hz, 1H, H_b), 6.99 (d, J 8.7 Hz, 2H, ArH) and 7.42 ppm (d, J 8.7 Hz, 2H, ArH); δ_C (75 MHz, $CDCl_3$): 40.6 [N(CH_3)$_2$, 42.9 (-CH_2), 55.4 (OCH_3), 59.5 (-CH), 108.7, 120.3, 124.9, 127.5, 130.8, 134.3, 142.2 and 149.7 ppm; ν_{max} ($CHCl_3$): 1641, 1378 and 1156 cm^{-1}; m/z: 309 (M^+) (found: C, 58.30; H, 6.16, N, 4.58 %. calc for $C_{15}H_{19}NO_4S$ (309); C, 58.23; H, 6.19, N, 4.53 %).

From reaction of **1c** with sulphene 6-[2-(4-chloro-phenyl)-vinyl]-2,2-dioxo-3,4-dihydro-2H-2λ^6-[1,2]oxathiin-4-yl}-dimethyl amine **2c** (85 %) was obtained as a light brown solid; δ_H (300 MHz, $CDCl_3$): 2.35 [s, 6H, -N(CH_3)$_2$], 3.26 (dd, J 11.4 and 13.2 Hz, 1H, -CH_2), 3.51 (ddd, J 0.9, 6.3 and 13.2 Hz, 1H, -CH_2), 4.12 (ddd, J 3.0, 6.6 and 11.4 Hz, 1H, -CH), 5.37 (d, J 2.7 Hz, 1H, H_c), 6.45 (d, J 15.6 Hz, 1H, H_a), 6.93 (d, J 15.6 Hz, 1H, H_b) and 7.29–7.37 ppm (m, 4H, ArH); δ_C (75 MHz, $CDCl_3$): 40.6 [N(CH_3)$_2$, 43.0 (-CH_2), 59.4 (-CH), 109.1, 120.2, 128.2, 129.0, 130.2, 134.0, 134.4 and 149.3 ppm; ν_{max} ($CHCl_3$): 1647, 1373 and 1156 cm^{-1}; m/z: 313 (M^+) (found: C, 53.66; H, 5.18, N, 4.41 %. calc. for $C_{14}H_{16}NClO_3S$ (313); C, 53.59; H, 5.14, N, 4.46 %).

From reaction of **1a** with sulphene 6-styryl-[1,2]oxathiine-

Table 4 Reactions of enaminones **1** and **5** with sulphene.

No.	Enaminones	Dienophile	Product	Yield/%
1	1a/1b/1c	sulphene [a]	2a/2b/2c	91/88/85
2	1a/1b/1c	sulphene [b]	3a/3b/3c	82/76/72
3	5a/5b/5c	sulphene [a]	7a/7b/7c	82/79/88
4	5a/5b/5c	sulphene [b]	3a/3b/3c	62/58/56

[a] Using 1.2 eq triethylamine.
[b] Using 3.0 eq triethylamine.

2,2-dioxide **3a** (82 %) was obtained as a colourless crystalline solid; δ_H (300 MHz, $CDCl_3$): 5.93 (d, J 6.9 Hz, 1H, H_c), 6.60 (d, J 10.5 Hz, 1H, H_e), 6.62 (d, J 15.6 Hz, 1H, H_a), 6.85 (dd, J 6.9 and 10.5 Hz, 1H, H_d) and 7.29–7.49 ppm (m, 6H, 5ArH and H_b); δ_C (75 MHz, $CDCl_3$): 103.7, 118.6, 119.1, 127.6, 128.9, 129.7, 134.4, 134.9, 136.1 and 156.3 ppm; ν_{max} ($CHCl_3$): 1628, 1541 and 1358 cm^{-1}; m/z: 234 (M^+) (found: C, 61.63; H, 4.27 %. calc. for $C_{12}H_{10}O_3S$ (234); C, 61.52; H, 4.30 %).

From reaction of **1b** with sulphene 6-[2-(4-methoxy-phenyl)-vinyl]-[1,2]-oxathiine-2,2-dioxide **3b** (76 %) was obtained as a colourless crystalline solid; δ_H (300 MHz, $CDCl_3$): 3.84 (s, 3H, $-OCH_3$), 5.88 (d, J 6.9 Hz, 1H, H_c), 6.47 (d, J 15.6 Hz, 1H, H_a), 6.56 (d, J 10.2 Hz, 1H, H_e), 6.81–6.92 (m, 3H, 2ArH and H_d), 7.29 (d, J 15.6 Hz, 1H, H_b) and 7.43 ppm (d, J 8.8 Hz, 2H, ArH); δ_C (75 MHz, $CDCl_3$): 55.3 ($-OCH_3$), 103.9, 118.6, 119.4, 127.3, 129.2, 133.9, 134.8, 135.6, 136.4 and 156.7 ppm; ν_{max} ($CHCl_3$): 1627, 1541, 1359 and 1182 cm^{-1}; m/z: 264 (M^+) (found: C, 59.15; H, 4.62 %. calc. for $C_{13}H_{12}O_4S$ (264); C, 59.08; H, 4.58 %).

From reaction of **1c** with sulphene 6-[2-(4-chloro-phenyl)-vinyl]-[1,2]-oxathiine-2,2-dioxide **3c** (72 %) was obtained as a colourless solid; δ_H (300 MHz, $CDCl_3$): 5.89 (d, J 6.9 Hz, 1H, H_c), 6.58 (d, J 10.5 Hz, 1H, H_e), 6.64 (d, J 15.9 Hz, 1H, H_a), 6.80–6.98 (m, 3H, 2ArH and H_d) and 7.01–7.48 ppm (m, 3H, 2ArH and H_b); δ_C (75 MHz, $CDCl_3$): 103.7, 118.5, 119.2, 126.3, 127.8, 129.9, 130.5, 133.8, 136.2 and 156.3 ppm; ν_{max} ($CHCl_3$): 1628, 1542, 1360 and 1183 cm^{-1}; m/z: 268 (M^+) (found: C, 53.72; H, 3.46 %. calc. for $C_{12}H_9ClO_3S$ (268); C, 53.64; H, 3.38 %).

From reaction of **5a** with sulphene (2,2-dioxo-6-styryl-3,4-dihydro-2H-2λ^6-[1,2]-oxathiin-4-yl)-phenylamine **7a** (82 %) was obtained as a yellow solid; δ_H (300 MHz, $CDCl_3$): 3.49 (dd, J 5.1 and 14.1 Hz, 1H, $-CH_2$), 3.67 (dd, J 5.7 and 14.1 Hz, 1H, $-CH_2$), 4.26 (bs, 1H, -CH), 4.87 (bs, 1H, -NH), 5.50 (d, J 4.2 Hz, 1H, olefinic), 6.47 (d, J 15.9 Hz, 1H, olefinic), 6.68–6.87 (m, 3H, ArH), 7.04 (d, J 15.9 Hz, 1H, olefinic) and 7.21–7.49 ppm (m, 7H, ArH); δ_C (75 MHz, $CDCl_3$): 48.5, 50.0, 106.8, 114.4, 119.4, 119.8, 127.1, 128.8, 128.9, 129.8, 132.5, 135.3, 144.7 and 150.2 ppm; ν_{max} ($CHCl_3$): 1155 and 1370 cm^{-1}; m/z: 327 (M^+) (found: C, 66.14; H, 5.29; N, 4.19 %. calc. for $C_{18}H_{17}NO_3S$ (327); C, 66.03; H, 5.23; N, 4.28 %).

From reaction of **5b** with sulphene (2,2-dioxo-6-styryl-3,4-dihydro-2H-2λ^6-[1,2]-oxathiin-4-yl)-(4-methoxy-phenyl) amine **7b** (79 %) was obtained as a yellow solid; δ_H (300 MHz, $CDCl_3$): 3.47 (dd, J 4.8 and 14.1 Hz, 1H, $-CH_2$), 3.63 (dd, J 6.8 and 14.1 Hz, 1H, $-CH_2$), 3.81 (s, 3H, $-OCH_3$), 4.23 (bs, 1H, -CH), 4.72 (bs, 1H, -NH), 5.51 (d, J 4.2 Hz, 1H, olefinic), 6.45 (d, J 15.9 Hz, 1H, olefinic), 6.69 (d, J 8.8 Hz, 2H, ArH), 6.88 (d, J 8.8 Hz, 2H, ArH), 7.03 (d, J 15.9 Hz, 1H, olefinic) and 7.25–7.43 ppm (m, 5H, ArH); δ_C (75 MHz, $CDCl_3$): 48.4, 50.1, 55.6, 107.2, 115.2, 116.7, 119.4, 127.0, 128.7, 128.9, 132.3, 135.3, 138.4, 149.9 and 153.8 ppm; ν_{max} ($CHCl_3$): 1156 and 1372 cm^{-1}; m/z: 357 (M^+) (found: C, 63.94; H, 5.28; N, 3.98 %. calc. for $C_{19}H_{19}NO_4S$ (357); C, 63.85; H, 5.36; N, 3.92 %).

From reaction of **5c** with sulphene (2,2-dioxo-6-styryl-3,4-dihydro-2H-2λ^6-[1,2]-oxathiin-4-yl)-p-tolyl amine **7c** (88 %) was obtained as a yellow solid; δ_H (300 MHz, $CDCl_3$): 2.34 (s, 3H, $-CH_3$), 3.46 (dd, J 4.9 and 14.1 Hz, 1H, $-CH_2$), 3.66 (dd, J 5.6 and 14.1 Hz, 1H, $-CH_2$), 4.27 (bs, 1H, -CH), 4.78 (bs, 1H, -NH), 5.50 (d, J 4.2 Hz, 1H, olefinic), 6.46 (d, J 15.9 Hz, 1H, olefinic), 6.78 (d, J 8.7 Hz, 2H, ArH), 6.99 (d, J 8.7 Hz, 2H, ArH), 7.02 (d, J 15.9 Hz, 1H, olefinic) and 7.13–7.47 ppm (m, 5H, ArH); δ_C (75 MHz, $CDCl_3$): 20.9, 48.5, 50.1, 106.9, 114.8, 118.9, 119.2, 125.2, 127.6, 128.6, 129.5, 132.6, 137.6, 147.1 and 152.8 ppm; ν_{max} ($CHCl_3$): 1155 and 1371 cm^{-1}; m/z: 341 (M^+) (found: C, 66.93; H, 5.53; N, 3.99 %. calc. for $C_{19}H_{19}NO_3S$ (341); C, 66.84; H, 5.61; N, 4.10 %).

6.4. General Procedure for Preparation of 1-Aryl-5-arylamino-penta-1,4-dien-3-one 5

A solution of **1** (5 mmol) and aryl amines **4** (aniline, p-anisidine and p-toluidine, (5 mmol)) in toluene (15 mL) was refluxed for 8–10 h. After completion (TLC), the solvent was evaporated under reduced pressure and the solid compounds thus obtained were recrystallized using a chloroform/hexane (1:5 v/v) mixture.

From reaction of **1a** with aniline 1-phenyl-5-phenylamino-penta-1,4-dien-3-one **5a** (80 %) was obtained as a yellow solid; δ_H (300 MHz, $CDCl_3$): 5.50 (d, J 7.5 Hz, 1H, H_a), 6.75 (d, J 15.9 Hz, 1H, H_c), 7.05 (d, J 15.9 Hz, 1H, H_d), 7.27-7.59 (m, 11H, 10ArH and H_b) and 12.16 ppm (d, J 11.7 Hz, 1H, -NH); δ_C (75 MHz, $CDCl_3$): 98.1, 116.2, 123.6, 127.6, 128.0, 128.8, 129.6, 129.7, 135.4, 139.6, 140.2, 144.4 and 189.1 ppm; ν_{max} ($CHCl_3$): 1620 and 1494 cm^{-1}; m/z: 249 (M^+) (found: C, 81.81; H, 6.10; N, 5.67 %. calc. for $C_{17}H_{15}NO$ (249); C, 81.90; H, 6.06; N, 5.62 %).

From reaction of **1a** with p-anisidine 1-(4-methoxy-phenyl-amino)-5-phenyl-penta-1,4-dien-3-one **5b** (77 %) was obtained as a yellow solid; δ_H (300 MHz, $CDCl_3$): 3.81 (s, 3H, $-OCH_3$), 5.42 (d, J 7.6 Hz, 1H, H_a), 6.84 (d, J 8.5 Hz, 2H, ArH), 6.98 (d, J 8.5 Hz, 2H, ArH), 7.19-7.58 (m, 8H, 5ArH, H_b, H_c and H_d) and 12.13 ppm (d, J 11.7 Hz, 1H, -NH); δ_C (75 MHz, $CDCl_3$): 55.4, 98.3, 116.3, 122.8, 125.4, 127.7, 128.6, 129.5, 131.8, 135.1, 139.2, 144.6, 145.8 and 189.2 ppm; ν_{max} ($CHCl_3$): 1624 and 1483 cm^{-1}; m/z: 279 (M^+) (found: C, 77.33; H, 6.09; N, 4.97 %. calc. for $C_{18}H_{17}NO_2$ (279); C, 77.40; H, 6.13; N, 5.01 %).

From reaction of **1a** with p-methylaniline 1-phenyl-5-p-tolyl-amino-penta-1,4-dien-3-one **5c** (88 %) was obtained as a light yellow solid; δ_H (300 MHz, $CDCl_3$): 2.39 (s, 3H, $-CH_3$), 5.47 (d, J 7.5 Hz, 1H, H_a), 6.88 (d, J 8.5 Hz, 2H, ArH), 6.99 (d, J 8.4 Hz, 2H, ArH), 7.20–7.59 (m, 8H, 5ArH, H_b, H_c and H_d) and 12.14 ppm (d, J 11.6 Hz, 1H, -NH); δ_C (75 MHz, $CDCl_3$): 20.9, 98.2, 116.3, 123.5, 125.8, 127.5, 128.6, 129.3, 129.8, 134.9, 140.1, 142.7, 145.1 and 189.3 ppm; ν_{max} ($CHCl_3$): 1625 and 1483 cm^{-1}; m/z: 263 (M^+) (found: C, 82.15; H, 6.45; N, 5.28 %. calc. for $C_{18}H_{17}NO$ (263); C, 82.10; H, 6.51; N, 5.32 %).

From reaction of **1b** with aniline 1-(4-methoxy-phenyl)-5-phenylamino-penta-1,4-dien-3-one **5d** (84 %) was obtained as a yellow solid; δ_H (300 MHz, $CDCl_3$): 3.83 (s, 3H, $-OCH_3$), 5.49 (d, J 7.8 Hz, 1H, H_a), 6.67 (d, J 15.9 Hz, 1H, H_c), 6.90 (d, J 8.4 Hz, 2H, ArH), 7.27-7.59 (m, 9H, 7ArH, H_b and H_d) and 12.13 ppm (d, J 11.4 Hz, 1H, -NH); δ_C (75 MHz, $CDCl_3$): 55.4, 98.3, 116.2, 122.9, 125.5, 127.9, 128.6, 129.3, 130.2, 134.8, 138.8, 139.9, 144.5 and 189.2 ppm; ν_{max} ($CHCl_3$): 1624 and 1480 cm^{-1}; m/z: 279 (M^+) (found: C, 77.51; H, 6.09; N, 5.11 %. calc. for $C_{18}H_{17}NO_2$ (279); C, 77.40; H, 6.13; N, 5.01 %).

From reaction of **1b** with p-anisidine 1-(4-methoxy-phenyl)-5-(4-methoxy-phenylamino)-penta-1,4-dien-3-one **5e** (90 %) was obtained as a golden yellow solid; δ_H (300 MHz, $CDCl_3$): 3.81 (s, 3H, $-OCH_3$), 3.83 (s, 3H, $-OCH_3$), 5.43 (d, J 7.6 Hz, 1H, H_a), 6.64 (d, J 15.9 Hz, 1H, H_c), 6.86–7.35 (m, 7H, 6ArH and H_d), 7.51 (d, J 8.7 Hz, 2H, ArH), 7.53 (d, J 7.6 Hz, H_b) and 12.18 ppm (d, J 11.6Hz, 1H, -NH); δ_C (75 MHz, $CDCl_3$): 55.3, 55.4, 98.1, 116.4, 121.2, 122.8, 124.9, 127.3, 130.6, 130.9, 133.8, 138.9, 142.9, 145.9 and 189.1 ppm; ν_{max} ($CHCl_3$): 1626 and 1477 cm^{-1}; m/z: 309 (M^+) (found: C, 73.63; H, 6.14; N, 4.60 %. calc. for $C_{19}H_{19}NO_3$ (309); C, 73.77; H, 6.19; N, 4.53 %).

From reaction of **1b** with p-methylaniline 1-(4-methoxy-phenyl)-5-p-tolylamino-penta-1,4-dien-3-one **5f** (79 %) was obtained as a yellow crystalline solid; δ_H (300 MHz, $CDCl_3$): 2.31 (s, 3H, $-CH_3$), 3.85 (s, 3H, $-OCH_3$), 5.46 (d, J 7.5 Hz, 1H, H_a), 6.65 (d, J 15.9 Hz, 1H, H_c), 6.89 (d, J 8.4 Hz, 2H, ArH), 6.98 (d, J 8.4 Hz, 2H, ArH), 7.13 (d, J 8.4 Hz, 2H, ArH), 7.35–7.53 (m, 3H, 2ArH and H_d),

7.55 (d, J 7.5 Hz, 1H, H_b) and 12.13 ppm (d, J 11.7 Hz, 1H, -NH); δ_C (75 MHz, $CDCl_3$): 21.0, 55.3, 98.2, 116.2, 123.7, 124.9, 126.7, 128.4, 129.2, 134.5, 141.1, 142.2, 142.8, 146.1 and 189.2 ppm; ν_{max} ($CHCl_3$): 1625 and 1475 cm^{-1}; m/z: 293 (M^+) (found: C, 77.72; H, 6.57; N, 4.72 %. calc. for $C_{19}H_{19}NO_2$ (293); C, 77.79; H, 6.53; N, 4.77 %).

Supplementary Material

The Cartesian coordinates and energies for all optimized structures are available as Supplementary Material online.

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