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A versatile route to benzodiazocine and spiropyran derivatives through chalcones

JOHNSON GEORGE[a], SAURABH SINGH[a],
RAHUL JOSHI[a] and RAMCHAND T PARDASANI[b,*]
[a]Department of Chemistry, University of Rajasthan, Jaipur 302 055, India
[b]Department of Chemistry, Central University of Rajasthan, Bandarsindri, Ajmer 305 802, India
e-mail: rtpardasani@curaj.ac.in

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Abstract. Syntheses of 3-(phenyl)-benzo[b]thiophene [2, 3-d][1,2] benzodiazocine derivatives have been accomplished by the reaction of 3-phenacylidine-2-benzo[b]thiophene-2-ones with *o*-phenylene diamine. The photolytic reaction with *trans*-stilbene resulted in the exclusive formation of spiro{2′,5′,6′-triphenyl-2H-pyran-4′,3}-benzo[b]thiophene-2-one derivatives. Theoretical calculations have been performed to study the mechanism and stereoselectivity of products. Good yield and broad scope of usable substrates of industrial relevance are other prominent features of the present methodologies.

Keywords. Thioisatin; chalcones; benzodiazocines; spiropyrans; DFT calculations; transition state.

1. Introduction

The thiophene ring system is probably the most well-known heterocycle, a common and important feature of various natural products and medicinal agents.[1] Its diketo derivative, benzo[b]thiophene-2,3-dione has an important applications in synthetic organic chemistry.[2] Incorporation of seven or eight-membered rings into the basic structural moiety may lead to pharmacologically active molecules.[3] A perusal of literature revealed that no chemistry of thioisatin-based benzodiazocine derivatives has been explored. For this purpose, the chalcones have been proved as potential building blocks for the synthesis of various heterocyclic systems and have shown a wide variety of biological activities.[4]

During the last three decades, the photochemistry of organic molecules has grown into an important and pervasive branch of organic chemistry. Photochemical cycloaddition provides one of the most efficient and versatile methods for the construction of carbo- and heterocycles of different sizes with high atom economy. Chow and co-workers have described the photocycloadditions of α-diketones,[5] yet the fascinating photochemistries of derivatives of benzo[b]thiophenes have remained largely unexplored. To make a contribution to these ongoing research fields connected with our interest in the synthesis of spiropyan compounds we here report a [4 + 2] photocycloaddition pathway for spiropyran heterocycles. Motivated by our recent works on 'stereoselectivity in [3 + 2] cycloaddition of azomethine ylides[6] and photochemistry of quinones[7] and their [2 + 2 / 3 + 2] photocycloadditions',[8] we have examined the feasibility of phenacylidines (chalcones) derived from thioisatin and a variety of ketones as building blocks for the construction of novel heterocyclic frameworks of possible industrial relevance and the results are presented here.

2. Experimental

2.1 *General procedures*

Melting points were determined in an open glass capillary and are uncorrected. The solvents were purified by standard procedures.[9] The IR spectra were recorded on Nicolet Magna IR TM model 550 in KBr pellets. The ^{1}H and ^{13}C NMR spectra were obtained on a JEOL AL-300 instrument at 300 and 75 MHz using $CDCl_3$ or DMSO-d_6 as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are given in δ ppm. Elemental analyses were performed by Perkin Elmer series C, H, N and S analyser-2400. Photochemical irradiation was conducted in a Heber multilamp photoreactor (Model: HML-COMPACT-SW-MW-LW888) consisting of a quartz/borosilicate reactor surrounded by 8 + 8 + 8 numbers of UV lamps (8 lamps can be operated at a time: either at 254 nm/312 nm/365 nm

*For correspondence

with 8 + 8 + 8 separate controls) permanently fixed inside the reaction chamber with built-in highly polished anodized aluminium reflector (85% reflection) so that UV rays are focused at the centre where the sample being kept. The reaction chamber is covered by reactor house which does not allow leakage of any UV irradiation. Thin-layer chromatography (TLC) was performed on alumina foil on Merck's Kiesel gel 60 F_{254} sheets, visualization was achieved at ultra fluorescence on an Indian Equipment Corporation equipment, IEC-312 at 354 nm. Column chromatography was carried over silica gel 60–120 mesh as adsorbent, using solvents of rising polarity.

2.2 *Computational details*

All computations were performed via different theoretical methods by using the Gaussian 03 suite of programs.[10] The optimization of the geometries and population analysis were carried out in detail by DFT-B3LYP/6-31G* molecular orbital calculations. Harmonic vibration frequencies of all stationary points have been computed to characterize them as energy minima (all frequencies are real) or transition states (one and only one imaginary frequency). An imaginary frequency has been obtained for each transition state which substantiates the actual formation of the transition state. Intrinsic reaction coordinates (IRC) calculations have been carried out to confirm the reaction pathway and the transition states.

2.2a *Synthesis of chalcones*: Acetophenone or its derivatives **2** (0.04 mol) were added consecutively with stirring to thioisatin **1** (0.04 mol) in the presence of catalytic amount of diethylamine. The mixture was refluxed for 8–10 h and the hydroxyl derivative obtained as precipitate was filtered off and recrystallized from ethanol. Then these derivatives undergo dehydration in the presence of AcOH–HCl mixture to give chalcones (**3a–h**).

2.2b *Physical and analytical data chalcone derivative **(3a)***: Yellow crystalline solid. Yield: 65%. m.p: 173–175°C. IR (KBr), 3040–3000 (Ar–H), 1720, 1645 (C=O), 630 (-C-S) cm^{-1}. ^1H NMR 300 MHz; $CDCl_3$; Me_4Si); δ 7.71–7.26 (m, 8H, Ar–H), 4.52 (s, 1H, C=CH), 2.42 (s, 3H, CH_3);^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 24.25 (CH_3), 114.08 (C=CH), 140.00–125.50 (Ar-C), 163.66 (C=O). Found: C, 72.16; H, 4.65; S, 11.18%. Calcd for $C_{17}H_{12}O_2S$: C, 72.83; H, 4.31; S, 11.44%.

2.3 *Synthesis of benzodiazocine derivatives*

The *o*-phenylene diamine (0.5 mmol) was added to the solution of chalcone **3** (0.5 mmol) in absolute ethanol (25 ml) at room temperature. Progress of the reaction was monitored on TLC plate. After 21 h colour of the reaction mixture changed from dark red to light which indicated completion of the reaction. The compound separated out was filtered, washed with cold petroleum ether and recrystallized from petroleum ether–chloroform mixture (3:1).

2.4 *Physical and analytical data of benzodiazocine derivatives*

2.4a *3-(Phenyl)-6-methyl benzo[b]thiophene[2,3-d][1,2] benzodiazocine **(4a)***: White powder. Yield: 56%. m.p: 227°C. IR (KBr), 3050–3000 (Ar–H), 1610, 1575 (C=N), 1550–1430 (C=C) cm^{-1}. ^1H NMR 300 MHz; $CDCl_3$; Me_4Si); δ 7.72–6.82 (m, 12H, Ar–H), 5.6 (s, 1H, C=CH), 2.4 (s, 3H, CH_3);^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 21.70 (CH_3), 124.20–145.90 (Ar–C), 155.50 (C=N), 159.20 (C=N). Found: C, 78.52; H, 4.67; N, 8.10; S, 8.93%. Calcd for $C_{23}H_{16}N_2S$: C, 78.38; H, 4.58; N, 7.95; S, 9.10%.

2.4b *3-(2-Methyl phenyl)-6-methyl benzo[b]thiophene [2,3-d][1,2]benzodiazocine **(4b)***: Fade brown solid. Yield: 62%. m.p: 198–200°C. IR (KBr), 3070–3010 (Ar–H), 1510, 1565 (C=N), 1530–1490 (C=C) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 7.60–6.80 (m, 11H, Ar–H), 5.7 (s, 1H, C=CH), 2.4 (s, 3H, CH_3), 2.5 (s, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 20.30 (CH_3), 22.70 (CH_3), 123.60–146.20 (Ar–C), 154.60 (C=N), 158.70 (C=N). Found: C, 78.20; H, 4.88; N, 7.81; S, 8.69% Calcd for $C_{24}H_{18}N_2S$: C, 78.66; H, 4.95; N, 7.64; S, 8.75%.

2.4c *3-(2-Pyridine)-6-methylbenzo[b]thiophene[2,3-d] [1,2]benzodiazocine **(4c)***: Fade yellow powder. Yield: 63%. m.p: 204–207°C. IR (KBr), 3050–3000 (Ar–H), 1620, 1580 (C=N), 1530–1450 (C=C) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 7.72–6.85 (m, 11H, Ar–H), 5.5 (s, 1H, C=CH), 2.4 (s, 3H, CH_3); ^{13}CNMR (75 MHz; $CDCl_3$; Me_4Si): δ 20.90 (CH_3), 126.20–148.50 (Ar–C), 155.50 (C=N), 158.60 (C=N). Found: C, 74.35; H, 4.20; N, 11.75; S, 9.20%. Calcd for $C_{22}H_{15}N_3S$: C, 74.76; H, 4.28; N, 11.89; S, 9.07%.

2.4d *3-(2-Thiophene)-6-methylbenzo[b]thiophene[2,3-d] [1,2]benzodiazocine **(4d)***: Brown solid. Yield: 59%. m.p: 196°C (decompose). IR (KBr), 3050–2990 (Ar–H), 1580, 1540 (C=N), 1510–1475 (C=C) cm^{-1}. ^1H

NMR (300 MHz; $CDCl_3$; Me_4Si); δ 8.25–6.86 (m, 10H, Ar–H), 5.50 (s, 1H, C=CH), 2.30 (s, 3H, CH_3), ^{13}CNMR (75 MHz; $CDCl_3$; Me_4Si): δ 21.30 (CH_3), 123.50–147.80 (Ar–C), 156.60 (C=N), 160.20 (C=N). Found: C, 69.95; H, 3.86; N, 7.92; S, 17.96%. Calcd for $C_{21}H_{14}N_2S_2$: C, 70.36; H, 3.94; N, 7.81; S, 17.89%.

2.4e *3-(2-Phenyl)-benzo[b]thiophene[2,3-d][1,2] benzodiazocine* ***(4e)***: Grey solid. Yield: 57%. m.p: 241°C (decompose). IR (KBr), 3050–3000 (Ar–H), 1570, 1550 (C=N), 1535–1515 (C=C) cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 7.90–6.85 (m, 13H, Ar–H), 5.6 (s, 1H, C=CH); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 126.00–144.00 (Ar–C), 155.90 (C=N), 160.50 (C=N). Found: C, 77.86; H, 4.26; N, 8.13; S, 9.39%. Calcd for $C_{22}H_{14}N_2S$: C, 78.08; H, 4.17; N, 8.28; S, 9.48%.

2.4f *3-(2-Methyl phenyl)-benzo[b]thiophene[2,3-d][1,2] benzodiazocine* ***(4f)***: Purple coloured powder. Yield: 52%. m.p: 203–205°C. IR (KBr), 3040–3010 (Ar–H), 1580, 1555 (C=N), 1530–1520 (C=C) cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 7.84–6.96 (m, 12H, Ar–H), 5.5 (s, 1H, C=CH), 2.3 (s, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 128.00–145.00 (Ar–C), 156.75 (C=N), 159.20 (C=N). Found: C, 77.98; H, 4.32; N, 7.75; S, 9.03%. Calcd for $C_{23}H_{16}N_2S$: C, 78.38; H, 4.58; N, 7.95; S, 9.10%.

2.4g *3-(2-Pyridine)benzo[b]thiophene[2,3-d][1,2] benzodiazocine* ***(4g)***: Grey powder. Yield: 65%. m.p: 175–178°C. IR (KBr) 3050–3000 (Ar–H), 1600, 1540 (C=N), 1520–1490 (C=C) cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 7.90–6.60 (m, 12H, Ar–H), 5.5 (s, 1H, C=CH); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ125.50–146.30 (Ar–C), 155.50 (C=N), 160.10 (C=N). Found: C, 74.23; H, 3.94; N, 12.30; S, 9.33%. Calcd for $C_{21}H_{13}N_3S$: C, 74.31; H, 3.86; N, 12.38; S, 9.41%.

2.4h *3-(2-Thiophene)benzo[b]thiophene[2,3-d][1,2] benzodiazocine* ***(4h)***: White powder. Yield: 63%. m.p: 171–174°C (decompose). IR (KBr), 3040–2980 (Ar–H), 1570, 1540 (C=N), 1520–1485 (C=C) cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 8.20–6.90 (m, 11H, Ar–H), 5.50 (s, 1H, C=CH); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 125.60–148.90 (Ar–C), 156.90 (C=N), 160.30 (C=N). Found: C, 69.66; H, 3.43; N, 8.20; S, 18.53%. Calcd for $C_{20}H_{12}N_2S_2$: C, 69.74; H, 3.51; N, 8.13; S, 18.62%.

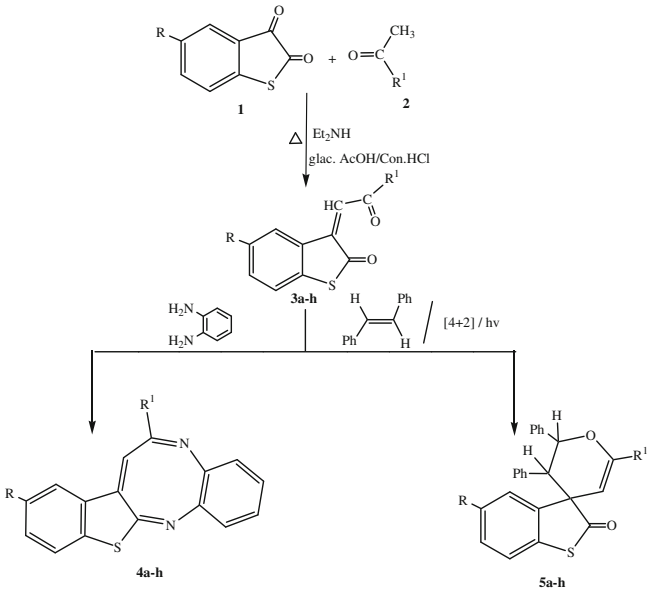
2.5 *Synthesis of spiropyran derivatives*

A solution of chalcone **3** (5 mmol) and *trans*-stilbene (5 mmol) in dry benzene (25 ml) was placed in quartz tube and irradiated at 312 nm under nitrogen atmosphere using Heber multilamp photoreactor for 16 h with magnetic stirring. After completion of the reaction which was monitored by thin-layer chromatography, the reaction mixture was concentrated under reduced pressure, furnished the product which was purified by column chromatography over silica gel.

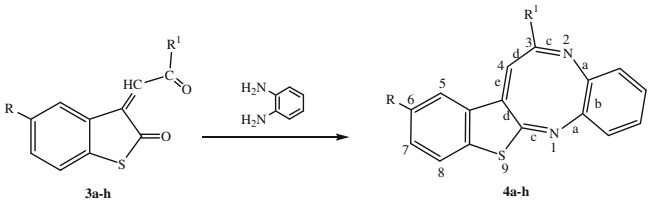
2.5a *Spiro{2′,5′,6′-triphenyl-2H-pyran-4′,3}-5-methylbenzo [b] thiophene-2-one* ***(5a)***: Brown solid. Yield: 56%. m.p: 221–224°C. IR (KBr), 3010–3043 (Ar–H), 1720 (C=O), 1610 (C=C), 608 (C-S) cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si); δ6.72–7.35 (m, 8H, Ar–H), 5.29 (d, 1H, CH), 4.98 (s, 1H, CH), 4.01 (d, 1H, CH), 2.21 (s, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ20.9 (CH_3), 58.90 (CH), 72.25 (CH), 81.60 (spiro C), 126.50–149.10 (Ar–C), 192.90 (C=O). Found: C, 81.15; H, 5.56; S, 6.78%. Calcd for $C_{31}H_{24}O_2S$: C, 80.84; H, 5.25; S, 6.96%.

2.5b *Spiro{2′(o-toluene)5′,6′-diphenyl-2H-pyran-4′,3}-5-methylbenzo[b] thiophene-2-one* ***(5b)***: Greenish yellow solid. Yield: 51%. m.p: 169°C. IR (KBr), 3000–3010 (Ar–H), 1740 (C=O), 1605 (C=C), 606 (C-S) cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 6.72–7.40 (m, 7H, Ar–H), 5.33 (d, 1H, CH), 5.02 (s, 1H, CH), 4.20 (d, 1H, CH), 2.29 (s, 3H, CH_3), 2.12 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, Me_4Si): δ 20.90 (CH_3), 22.52 (CH_3), 57.52 (CH), 71.60 (CH), 83.00 (spiro C), 125.90–148.20 (Ar–C), 191.20 (C=O). Found: C, 81.15; H, 5.56; S, 6.78%. Calcd for $C_{32}H_{26}O_2S$: C, 80.98; H, 5.52; S, 6.76%.

2.5c *Spiro{2′(o-pyridine)-5′,6′(diphenyl)-2H-pyran-4′,3}-5-methylbenzo[b] thiophene-2-one* ***(5c)***: Grey solid. Yield: 50%. m.p: 172–174°C. IR (KBr), 3006–3033 (Ar–H), 1725 (C=O), 1608 (C=C), 1600 (C=N) 610 (C-S) cm^{-1}. ^{1}H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 6.65–7.21 (m, 7H, Ar–H), 5.65 (d, 1H, CH), 5.10 (s, 1H, CH), 4.26 (d, 1H, CH), 2.30 (s, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 20.13 (CH_3), 55.50 (CH), 70.23 (CH), 83.44 (spiroC), 124.60–154.70 (Ar–C), 190.90 (C=O). Found: C, 78.33; H, 5.21; N, 3.20; S, 6.81%. Calcd for $C_{30}H_{23}NO_2S$: C, 78.06; H, 5.02; N, 3.03; S, 6.95%.



Scheme 1. Synthetic route for benzodiazocines and spiropyrans from thioisatins.



Scheme 2. Synthesis of benzodiazocines.

2.5d *Spiro{2′(o-thiophene)-5′,6′-diphenyl-2H-pyran-4′,3}-5-methylbenzo[b] thiophene-2-one* ***(5d)***: White powder. Yield: 55%. m.p: 201–204°C. IR (KBr), 3004–3033 (Ar–H), 1725 (C=O), 1605 (C=C), 612, 620 (C-S) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 6.72–7.35 (m, 6H, Ar–H), 5.32 (d, 1H, CH), 4.95 (s, 1H, CH), 4.06 (d, 1H, CH), 2.26 (s, 3H, CH_3); ^{13}CNMR (75 MHz; $CDCl_3$; Me_4Si): δ 21.9 (CH_3), 57.60 (CH), 73.33 (CH), 82.50 (spiro C), 127.50–144.20 (Ar–C), 191.70 (C=O). Found: C, 81.15; H, 5.56; S, 6.78%. Calcd for $C_{29}H_{22}O_2S_2$: C, 74.65; H, 4.75; S, 13.74%.

2.5e *Spiro{2′,5′,6′-triphenyl-2H-pyran-4′,3}-benzo[b] thiophene-2-one* ***(5e)***: Light yellow solid. Yield: 56%. m.p: 221–224°C. IR (KBr), 3015–3044 (Ar–H), 1725 (C=O), 1620 (C=C), 609 (C-S) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 6.75–7.32 (m, 9H, Ar–H), 5.29 (d, 1H, CH), 4.93 (s, 1H, CH), 4.18 (d, 1H, CH); ^{13}C NMR (75 MHz; $CDCl_3$, Me_4Si): δ 59.55 (CH), 71.33 (CH), 80.80 (spiro C), 124.60–147.10 (Ar–C), 193.50 (C=O). Found: C, 80.81; H, 5.56; S, 7.10%. Calcd for $C_{30}H_{22}O_2S$: C, 80.69; H, 5.25; S, 7.18%.

2.5f *Spiro{2′(o-toluene)5′,6′-diphenyl-2H-pyran-4′,3}-benzo[b]thiophene-2-one* ***(5f)***: Blackish brown solid. Yield: 58%. m.p: 241°C (decompose). IR (KBr), 3004–3018 (Ar–H), 1744 (C=O), 1611 (C=C), 610 (C-S) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 6.80–7.71 (m, 8H, Ar–H), 5.35 (d, 1H, CH), 5.09 (s, 1H, CH), 4.15 (d, 1H, CH), 2.29 (s, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 22.60 (CH_3), 57.52 (CH), 72.00 (CH), 83.50 (spiro C), 124.45–145.25 (Ar–C), 190.10 (C=O). Found: C, 81.11; H, 5.33; S, 6.79%. Calcd for $C_{31}H_{24}O_2S$: C, 80.84; H, 5.25; S, 6.96%.

Table 1. Physical data of chalcone derivatives (**3a–h**).

Entry	Product	R	R^1	Time (h)	M.p. (°C)	Yield (%)
1	**3a**	CH_3	C_6H_5	13	173–175	65
2	**3b**	CH_3		15	195–196	68
3	**3c**	CH_3		17	188	59
4	**3d**	CH_3		10	201–205	70
5	**3e**	H	C_6H_5	14	210–212	58
6	**3f**	H		10	156–157	65
7	**3g**	H		13	180–182	63
8	**3h**	H		12	232	71

Table 2. Physical data of benzodiazocine derivatives (**4a–h**).

Entry	Product	R	R^1	Time (h)	M.p. (°C)	Yield (%)
1	**4a**	CH_3	C_6H_5	16	227	56
2	**4b**	CH_3		20	198–200	62
3	**4c**	CH_3		18	204–207	63
4	**4d**	CH_3		28	196(d)	59
5	**4e**	H	C_6H_5	25	241(d)	57
6	**4f**	H		21	203–205	52
7	**4g**	H		20	175–178	65
8	**4h**	H		23	171–174	63

2.5g *Spiro{2′(o-pyridine)-5′,6′(diphenyl)-2H-pyran-4′,3}-benzo[b]thiophene-2-one* ***(5g)***: Brown solid. Yield: 54%. m.p: 192°C. IR (KBr), 3010–3040 (Ar–H), 1722 (C=O), 1605 (C=C), 1590 (C=N) 610 (C-S) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 6.60–7.29 (m, 8H, Ar–H), 5.60 (d, 1H, CH), 5.14 (s, 1H, CH), 4.22 (d, 1H, CH), 2.36 (s, 3H, CH_3); ^{13}C NMR (75 MHz; $CDCl_3$; Me_4Si): δ 55.65 (CH), 70.95 (CH), 85.20 (spiro C), 126.00–153.10 (Ar–C), 192.10 (C=O). Found: C, 77.64; H, 4.91; N, 3.08; S, 7.20%. Calcd for $C_{29}H_{21}NO_2S$: C, 77.83; H, 4.73; N, 3.13; S, 7.16%.

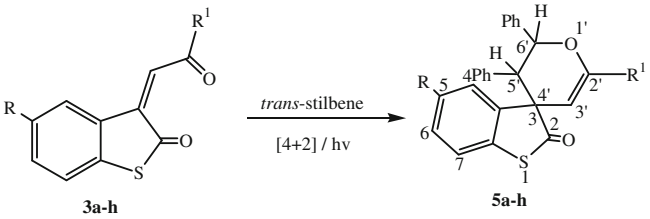
2.5h *Spiro{2′(o-thiophene)-5′,6′-diphenyl-2H-pyran-4′,3}-benzo[b]thiophene-2-one* ***(5h)***: Yellowish white powder. Yield: 57%. m.p: 212–214°C. IR (KBr), 3010–3025 (Ar–H), 1730 (C=O), 1608 (C=C), 612, 620 (C-S) cm^{-1}. ^1H NMR (300 MHz; $CDCl_3$; Me_4Si); δ 6.75–7.45 (m, 7H, Ar–H), 5.35 (d, 1H, CH), 4.95 (s, 1H, CH), 4.10 (d, 1H, CH), 2.33 (s, 3H, CH_3);^{13}CNMR (75 MHz; $CDCl_3$; Me_4Si): δ 57.60 (CH), 73.33 (CH), 82.00 (spiro C), 130.50–142.00 (Ar–C), 192.15 (C=O). Found: C, 81.15; H, 5.56; S, 6.78%. Calcd for $C_{28}H_{20}O_2S_2$: C, 74.31; H, 4.45; S, 14.17%.

3. Results and discussion

The first step in this synthesis involved Knoevanagel condensation between the thioisatin (**1**) and acetophenone or its derivatives (**2**) in the basic medium (diethylamine) to give the aldol products, which then dehydrated easily by using con.HCl–AcOH mixture to yield the α, β-unsaturated carbonyl compounds (3-phenacylidine-2-benzo[b]thiophene-2-ones)[11] (**3a–h**), commonly known as chalcones, in 58–71% yield (scheme 1). The structures of these products were established by physical (table 1) and spectral data.

The cyclocondensation reaction of appropriate 3-phenacylidine-2-benzo[b]thiophene-2-ones (**3a–h**) with *o*-phenylene diamine in ethanol at room temperature for 21 h resulted in the exclusive formation of the benzodiazocine products in 52–65% yield (**4a–h**) (scheme 2). The products were unambiguously confirmed by spectral methods. Absence of >C=O groups and appearance of >C=N groups in IR in the range of 1595–1600 cm^{-1}, appearance of olefinic proton (C=CH) in the ^1H NMR spectra at ~5.6 ppm and disappearance of both >C=O groups in ^{13}C NMR were decisively indicative of products as 3-aryl-benzo[b]thiophene[2,3-d][1,2] benzodiazocine (**4a–h**). The physical data are presented in table 2.

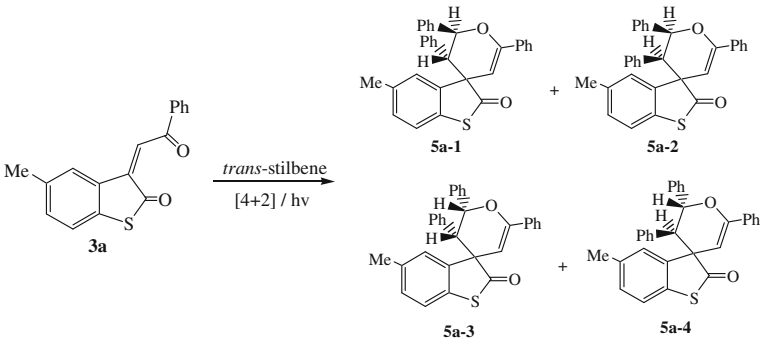
The photocycloaddition reaction of chalcones with *trans*-stilbene was carried out under nitrogen atmosphere in dry benzene with constant stirring in Heber photoreactor with medium pressure mercury arc lamp at 312 nm. The photochemical reaction was continued until no further thioisatin was consumed (scheme 3).



Scheme 3. Synthesis of spiropyrans.

Table 3. Photocycloadducts (**5a–h**).

Entry	Product	R	R^1	Time (h)	M.p. (°C)	Yield (%)
1	**5a**	CH_3	C_6H_5	24	221–224	56
2	**5b**	CH_3		27	169	51
3	**5c**	CH_3		24	172–174	50
4	**5d**	CH_3		21	201–204	55
5	**5e**	H	C_6H_5	27	221–224	56
6	**5f**	H		27	241	58
7	**5g**	H		24	192	54
8	**5h**	H		21	212–214	57



Scheme 4. Possible stereoisomers for the cycloadduct **5**.

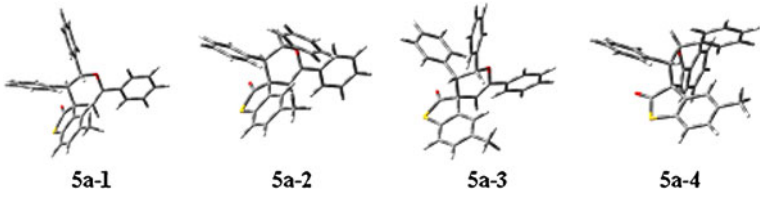
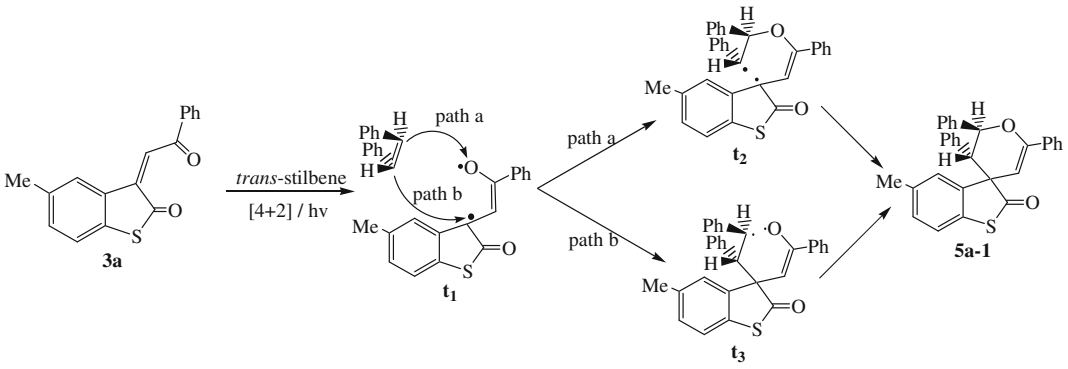


Figure 1. Optimized geometries of possible stereoisomers.

Table 4. Total energy of possible stereoisomers.

Stereoisomers	**5a–1**	**5a–2**	**5a–3**	**5a–4**
Energy (kcal/mol)	−1094622.60	−1094616.33	−1094620.47	−1094615.89



Scheme 5. Mechanism of photocycloaddition reaction.

Table 5. Energy of reactants, biradical intermediates and transition states.

Species	**3a**	***trans*-stilbene**	t_2	t_3	**5a–1**
Energy (kcal/mol)	−755316.09	−339300.93	−1094575.19	−1094568.95	−1094622.60

Subsequently, the reaction mixture was evaporated and the crude products were purified by column chromatography over silica gel to afford photo-adducts (**5a–h**) in 50–58% yield (table 3).

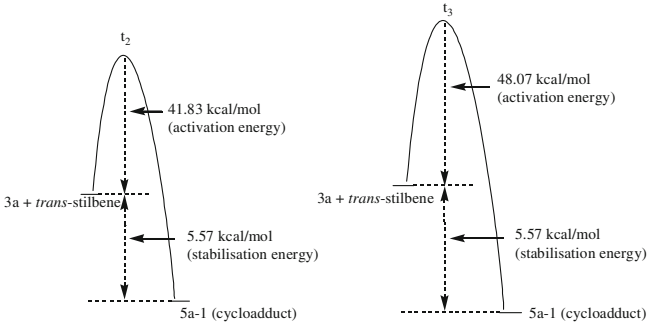


Figure 2. Energy profile diagram for the formation of cycloadduct **5a–1**.

The structure of the photocycloadducts (**5a–h**) has been ascertained from their spectral data. Absence of one >C=O group in IR/^{13}C NMR as well as appearance of spirocarbon at ∼ δ 81.0 ppm in ^{13}C NMR decisively confirmed the formation of spiro{2′,5′,6′-triphenyl-2H-pyran-4′,3}-benzo[b]thiophene-2-one (**5a–h**) products.

3.1 *Regio- and stereoselectivity of photocycloaddition*

The regio- and stereoselectivity of the [4 + 2] photocycloaddition reaction has been investigated in detail by DFT molecular orbital calculations. In this study, photocycloaddition of chalcone **3a** with *trans*-stilbene is chosen as the model reaction. The attack of *trans*-stilbene on chalcone **3a** may result in the formation of four isomers **5a–1** to **5a–4** (scheme 4).

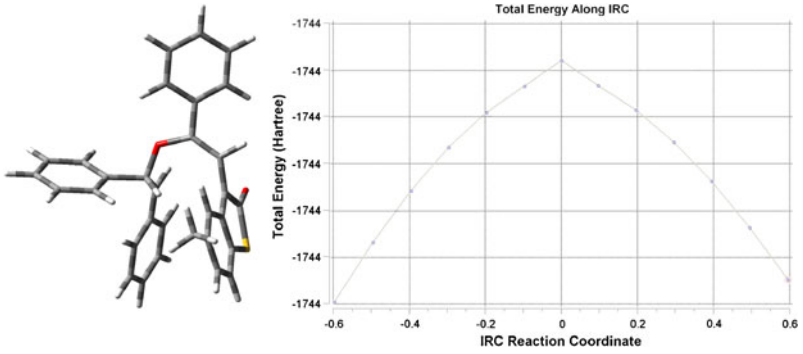


Figure 3. (**a**) Optimized geometry of t_2, (**b**) IRC plot for the transition state t_2.

The geometry and energy of all four possible stereoisomers have been optimized at B3LYP/6-31G* level of theory and are shown in figure 1. The relative energies leading to structural and stereoelectronic differences are presented in table 4.

It is evident from table 4. that the stereoisomer (**5a–1**) is thermodynamically more stable than the other stereoisomers. The proximity of the bulky phenyl groups to ring system may be attributed to the relative destabilization of the remaining (**5a–2** to **5a–4**) stereoisomers.

3.2 *Mechanism of photocycloaddition reaction*

The next task was to illustrate a feasible mechanism for the formation of spiropyran (**5a–1**). A plausible mechanism is depicted in scheme 5.

Generally, the photocycloadditions of α, β-unsaturated ketones occur via triplet excited states[11] and the present photocycloaddition reaction is also proposed to proceed through a triplet biradical intermediate, $\mathbf{t}_1$. The attack of *trans*-stilbene on triplet biradical ($\mathbf{t}_1$) can take place via two different pathways. In path '**a**' the attack of *trans*-stilbene may take place on the oxygen radical generating intermediate triplet biradical $\mathbf{t}_2$ and in path '**b**' *trans*-stilbene may first attack on the carbon radical yielding another intermediate triplet biradical $\mathbf{t}_3$. Further, both $\mathbf{t}_2$ and $\mathbf{t}_3$ may cyclise to give the photocycloadduct **5a–1**. All the ground state reactant and products and intermediate triplet biradicals as well as transition states have been optimized at B3LYP/6-31G* level to estimate their energy and to predict the feasible mechanistic pathway. The results are summarized in table 5. It is evident from these calculations that triplet radical $\mathbf{t}_2$ is thermodynamically more stable than $\mathbf{t}_3$. The extended conjugation of carbon radical with the labile π-electron pair as well as phenyl group may be attributed to its greater stability.

The potential energy barrier for reactant $\mathbf{t}_2 \rightarrow$ **5a–1** conversion is 41.83 kcal/mol while that of $\mathbf{t}_3 \rightarrow$ **5a–1** conversion is 48.07 kcal/mol (figure 2). This clearly indicates that the photocycloaddition proceeds via the primary biradical $\mathbf{t}_2$ to yield the final cycloadduct **5a–1**. The optimized geometry of the biradical $\mathbf{t}_2$ and the corresponding IRC plot for the formation of **5a–1** is shown in figure 3.

4. Conclusions

A series of novel benzodiazocine and spiropyran derivatives have been synthesized by cyclocondesation and [4 + 2]-photocycloadditions of chalcones with *o*-phenylene diamine and *trans*-stilbene. The electronic delocalizations, mechanism and stereochemistry of the reaction has been established theoretically by B3LYP/6-31G* method.

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