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PAPER

Non-catalytic approach to the synthesis of partially reduced 'S' shaped dioxathia- and oxadithiahelicenes through base induced inter- and intramolecular C–C bond formation†

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An efficient and convenient route for the construction of helical 'S' shaped dioxathia- and oxadithiahelicenes with oxygen and sulfur atoms located in the middle of the outer helix has been developed through base induced inter- and intramolecular C–C bond formation from the reaction of 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles with 3,4-dihydro-2*H*-benzo[*b*]oxepin-5(2*H*)-ones, 3,4-dihydrobenzo[*b*]thiepin-5(2*H*)-one and thiochroman-4-ones separately. Quantum chemical calculations have also been carried out to explore the geometries and electronic structures of newly synthesized compounds to envisage the pathway for interconversion of both atropisomers. The determination of helicity parameters and configurational stability demonstrate that the energy barrier is strongly dependent on the nature of hetero-atoms present.

Introduction

Helicenes are three-dimensional polycyclic, thermally stable π conjugated *ortho*-annulated aromatic ring systems with inherent chirality. The unique physical and chemical properties of these non-planar helical molecules urged continued interest in the fascinating field of helicene chemistry.[1] Besides, optical[2] and electronic[3] properties, the inherent chirality[4] of helicenes has led to their promising applications in asymmetric catalysis,[5] asymmetric molecular recognition,[6] liquid crystals,[7] dyes,[8,9] sensors,[8,9] electrostatic switches,[10] polymer synthesis[7,11,12] and circularly-polarized luminescent devices.[7,11,12] The determination of racemisation barrier (RB) reflects the repulsive interaction between terminal rings and is a crucial indicator of helicity. The RBs in case of carbohelicenes, depend upon several factors such as the number of *ortho*-annulated aromatic rings and substituents present at helix sites and the modulation of steric hindrance on the terminal positions of the inner helix.[8,13] Partial reduction in the molecule also modulates the racemisation barrier. In fact, the nature and position of heteroatoms also influence the helicity parameters such as bond lengths, dihedral angles and configurational stability. Thus, [4]carbohelicenes are quite stable at room temperature even with the introduction of a bulky substituent on the terminal rings of the inner helix.[9,14] The introduction of methyl substituent at position 1 increases configurational stability similar to the effect of an additional aromatic ring.

An overview of literature over the last century has highlighted carbohelicenes as helical frameworks. Helicenes have classically been synthesized by oxidative photocyclization of bis(stilbenes)[10b,15] with poor regio-control. The requirement of highly substituted helicenes for various applications has led to the development of several novel approaches to their syntheses. Katz *et al.*[16,17] have described an access to the synthesis of helical bisquinones through Diels–Alder reaction. The transition-metal catalyzed [2 + 2 + 2]cycloisomerization of triynes and dienetriynes,[16,17] was found as alternative routes to the synthesis of this class of compounds. In 2006, Collins *et al.* published a new synthetic route to highly substituted helicenes with different frameworks by ring closing olefin metathesis.[18,19] An intramolecular Pd-catalyzed C–C bond formation[20] and Friedel–Crafts cyclization strategies[21] have also been followed for the construction of helicenes of different structural frameworks. Recently, heterohelicenes[4,22] (*i.e.* oxa, aza, thia, oxathia) have emerged as extremely attractive molecules because of their photorefractive properties.[23] Karikomi *et al.*[24] have developed stereoselective synthesis of [5]helicenes by oxy-Cope rearrangement as key step. Recently, Genetet *et al.*[25] have reported an elegant enantioselective synthesis of helicenes through chirality transfer from an enantiopure tether to a flexible [5]helicene backbone.

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† Electronic supplementary information (ESI) available: Optimized structures along with the Cartesian coordinates (**4f**.xyz, **4f**TS.xyz, **9c**.xyz, **9c**Ts.xyz, **9d**.xyz, **9d**ts.xyz) and copies of IR, HRMS, ^{1}H NMR, ^{13}C NMR spectra of compounds. CCDC reference numbers 831578 (**4f**), 831579 (**9c**) and 831577 (**9d**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1ob06091k

The synthesis of regio-defined heterohelicenes is of significant interest.[4,18] Regardless of recent significant progress in helicene chemistry, development of new, short, efficient routes are still desired to allow further functionalization to build additional rings.

Results and discussion

The fascinating architecture of helicenes and their vivid unexplored potential applications in material science stimulated us to devise an economical, efficient and short synthesis through base induced inter- and intramolecular C–C bond formation from the reaction of suitably functionalized 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[3,4-*c*]pyran-3-carbonitriles (**4**) with 3,4-dihydro-2*H*-benzo[*b*]oxepin/thiepin-5(2*H*)-ones[29] (**5**), a feasible concept exhibiting a high degree of synthetic flexibility for the construction of partially reduced dioxathia- and oxadithahelicenes, not reported so far. The crux of methodology lies in non-catalytic synthesis of various partially reduced dioxthia- and oxadithiahelicenes, endowed with halo, amino and nitrile functionalities, transformable to other groups either catalytically or chemically. Besides this, the methodology also provides an avenue for the synthesis of partially reduced helicenes, not easily obtainable either chemically or catalytic regioselective hydrogenation.

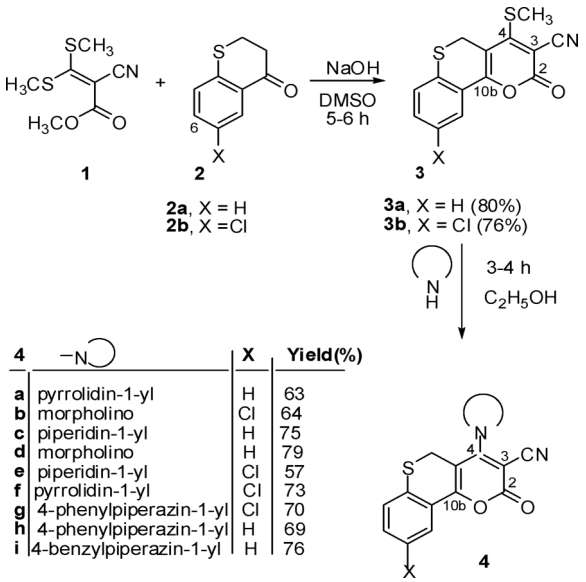
It has been reported[26] that the planarity of the rings in polycyclic systems induces carcinogenicity which is either reduced or destroyed by distortion in the planarity of the rings. The partial reduction is also one of the ways for disrupting the planarity of rings. Thus, we developed an elegant synthetic route to induce distortion in the planarity of the rings through partial reduction, employing partially reduced precursors.

As apparent from the structure of 4-methylthio-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (**3a,b**), these were obtained from the reaction of thiochroman-4-ones (**2**) and methyl 2-cyano-3,3-dimethylthioacrylate[27] (**1**). Amination[28] of **3** with *sec*-amine in boiling ethanol resulted in 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (**4**) and were used as precursors for the ring transformation reactions (Scheme 1).

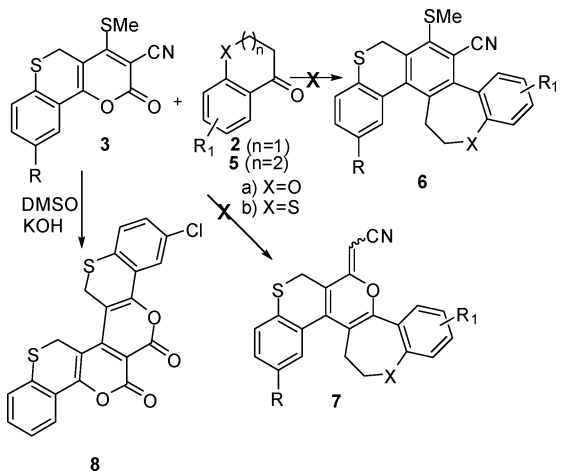
The synthetic potential of 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (**4**) is enormous. The unique structural features and the presence of functional groups were exploited for the construction of a variety of heteroarenes of helical shape.

It is evident from the topography of the thiochromeno[4,3-*b*]pyran-3-carbonitriles **3** and **4** that the positions C2, C4 and C10b are electron deficient, in which the latter is particularly so, and prone to nucleophilic attack because of an extended conjugation and the presence of an electron-withdrawing CN substituent at position 3 of the lactones **3**, **4**. Both the lactones (**3**, **4**) are very useful synthons for the ring transformation reactions. The basic difference in both the lactones lies in the nature of substituent present at position 4. In the case of lactone **3** the $–SCH_3$ substituent at position 4 is more labile and highly vulnerable to nucleophilic attack compared to the *sec*-amino substituent in **4**.

However, the reaction of an equimolar mixture of 4-methylthio-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (**3**) and 3,4-dihydro-2*H*-benzoxapin-5-one (**5**) did not deliver the expected products **6** and **7** (Scheme 2) but *in lieu* produced **8**. We performed several reactions to make more derivatives of **8** but



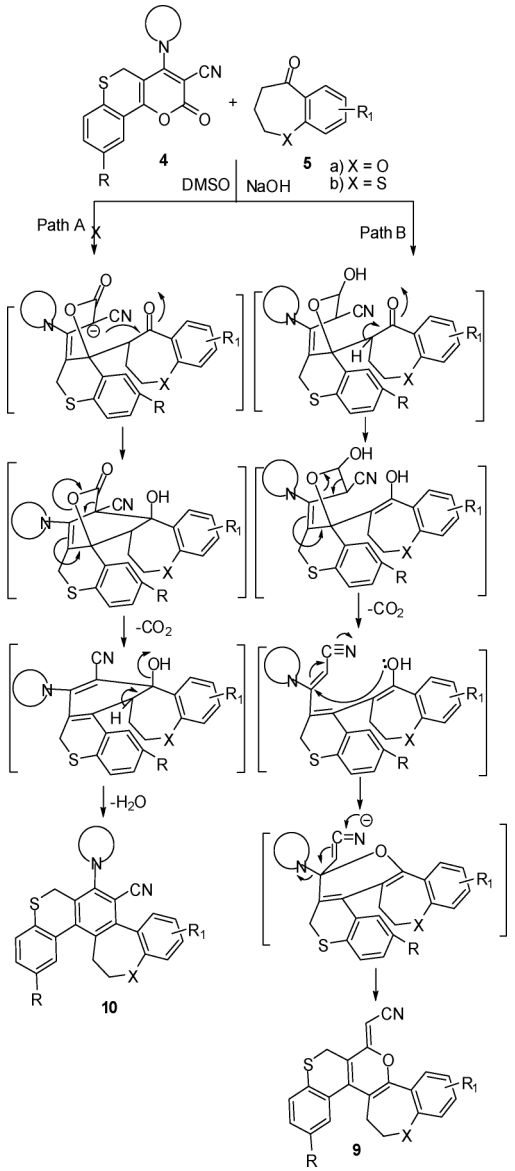
Scheme 1 Synthesis of 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno-[4,3-*b*]pyran-3-carbonitriles (**4**).



Scheme 2

unfortunately only one compound was isolated and characterized. Nevertheless, the reaction initiated with attack of nucleophile at position 4 rather than at C10b, followed by ring closure involving cyano function to yield **8**. The only option to obtain the desired product **6** was to reduce the electrophilicity of the C-4 position by replacing $–SCH_3$ by a *sec*-amino substituent to facilitate the attack of carbanion at C-10b.

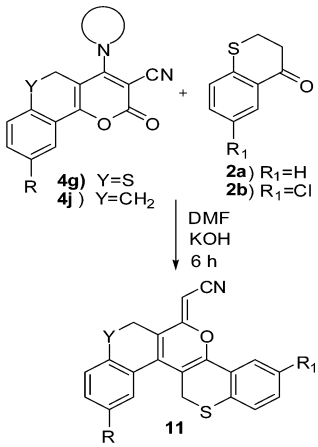
Thus, an equimolar mixture of the 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (**4**), 3,4-dihydro-2*H*-benzo[*b*]oxepin/thiepin-5(2*H*)-ones[29] (**5**) and powdered NaOH as a base was stirred for 14 h in DMSO with continuous monitoring of the reaction progress by TLC. The usual workup and purification on Si gel column chromatography exclusively gave (*Z*)-2-(1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-*d*]benzo[*b*]oxepine(2*H*)-ylidene)acetonitriles (**9**), following path **B**, without formation of another expected product 9-*sec*-amino-1,2-dihydro-10*H*-thiochromeno[4,3-*e*]dibenzo[*b*,*d*]oxepine-9-carbonitriles (**10**) through path **A**, as depicted in Scheme 3.



Scheme 3 A plausible mechanism for the synthesis of the (*Z*)-2-(1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-*d*]benzo[*b*]oxepin-(2*H*)-ylidene)acetonitriles (**9**) and 9-*sec*-amino-1,2-dihydro-10*H*-thiochromeno[4,3-*e*]dibenzo[*b*,*d*]oxepine-9-carbonitriles (**10**).

In order to study the effect of the 4-*sec*-amino substituent in **4** on the yield of the dioxathia- (**9a–c**) and dithia- oxahelicenes (**9d,e**), 4-pyrrolidin-1-yl-, morpholin-4-yl-, piperidin-1-yl- and (4-arylpiperazin-1-yl)-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]-3-carbonitriles were used as precursors (Table 1). However, only 4-(morpholin-4-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (**4d**) with thiochroman-4-ones (**2**) gave exclusively (*Z*)-2-(1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-*d*]benzo[*b*]oxepine(2*H*)-ylidene)acetonitriles (**9**) as evidenced from the single-crystal X-ray diffraction study of **9c**.

To generalize the reaction, the ring transformation of 9-chloro-2-oxo-4-(4-phenylpiperazin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (**4g**) with 6-chlorothiochroman-4-one (**2b**) was carried out which gave product **11a** under analogous reaction conditions. Similarly, the ring transformation of 4-(4-methylpiperazin-1-yl)-2-oxo-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitrile (**4j**) by thiochroman-4-ones (**2**) gave products **11b–c**, analogous to **9a** as shown in Scheme 4.



11	R	R_1	Y	−N◯	Yield (%)
a	Cl	H	S	4-phenylpiperazin-1-yl	25
b	H	H	CH_2	4-methylpiperazin-1-yl	30
c	H	Cl	CH_2	4-methylpiperazin-1-yl	35

Scheme 4 2-(7,8-Dihydrobenzo[*f*]thiochromeno[4,3-*c*]isochromen-6-(13*H*)-ylidene)acetonitriles **11a–c**.

Crystal structures and quantum chemical studies

Crystals of X-ray quality for **4f**, **9c** and **9d** were obtained by slow evaporation of the solvent (dichloromethane–hexane) at room temperature. The molecular structures of the compounds with arbitrary numbering are presented in Fig. 1, illustrating the non-planar, helically distorted conformation of the molecules. Compound **4f** crystallizes in the $Pca2_1$ space group with eight molecules in the orthorhombic unit cell. The least-square plane calculations reveal that only ring **A** is planar, while the other rings **B** and **C** are non-planar. The non-planarity of the six membered ring **B** is attributed to the presence of sp^3 hybridized C12 and S1 atoms. In the case of the ring **C**, the deviation from planarity is because of the presence of one sp^3 hybridized oxygen atom O1. The deviations of S1 and C12 from the plane of ring **B** are –0.159 and +0.694 Å, respectively, whereas the oxygen atom O1 deviates by –0.178 Å from the plane of the ring **C**. The torsion angles C5–C6–C7–O1 and C6–C7–O1–C8 are 16.21 and 171.73° respectively.

Compounds **9c** and **9d** crystallized in $P2_1/n$ and $P2_1/c$ space groups, respectively, with four and eight molecules in the monoclinic unit cells, respectively. In both the compounds, the least-square plane calculation from X-ray crystallographic data indicates that the fully unsaturated rings **A**, **C** and **E** are nearly planar. The rings **B** adopt half chair conformation because of the presence of the sp^3 hybridized sulfur atom. The seven-membered ring **D** also possesses puckered conformations because of the presence of the S1 atom in **9d** and O2 atom in the case of **9c**. The average mean plane angle for the twist between the rings **A** and **C** is 38.69° for **9d** and 36.49° for **9c**. The smaller twist angle of **9c** as compared to **9d** may be attributed to the presence of the smaller O2 atom in ring **D**. The dihedral angle between the rings **C** and **E** in **9d** is 44.95°, while in **9c** is merely 4.62°. The appreciably large

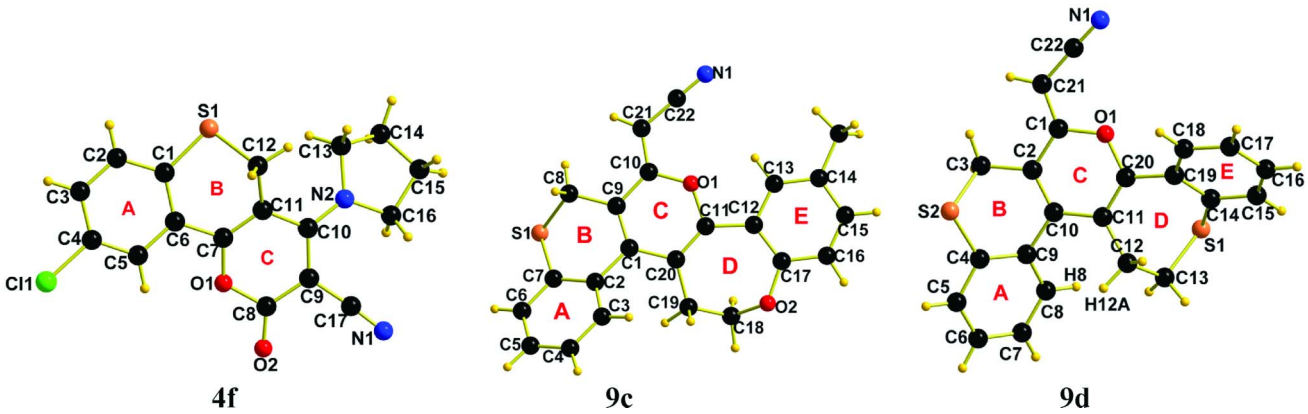
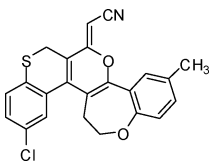
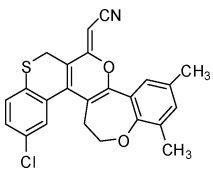
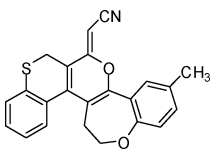
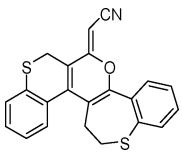
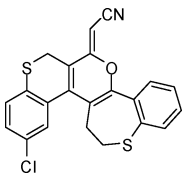


Fig. 1 Perspective view of **4f**, **9c** and **9d** with atom numbering scheme.

Table 1 Reactants **4** used for the preparation of **9** with their yields and melting points

9	Reactant 4	Product 9	Mp/°C	Yield (%)
9a	**4e** **4f**		220	95 80
9b	**4e** **4f**		186	58 57
9c	**4c**		164	92
9d	**4d**		144	40
9e	**4e**		110	38

dihedral angle in the **9d** is because of the large S1–C14 bond length 1.777(2) Å, while for **9c** the O2–C17 bond length is 1.3786(16) Å. Hence, it can be concluded that exchange of the heteroatom in the seven-membered ring **D** changes the twist/dihedral angle and thereby influences the helicity of the molecule. The distance between the non-bonded carbon atoms C8 and C12 in **9d** is 3.049 Å, whilst the distance in **9c** between C3 and C19 is 2.970 Å, which is shorter by ~0.4 Å as compared to van der Waals radii of two carbon atoms, and is responsible for a molecular distortion. For **9d** the torsion angles C8–C9–C10–C11, C9–C10–C11–C12 and C10–C11–C12–C13 are −38.71, −10.86 and 110.52°, respectively. For **9c** the torsion angles C3–C2–C1–C20, C2–C1–C20–C19 and C1–C20–C19–C18 are 38.01, 12.90 and 152.41°, respectively.

In order to gain deeper insight into the stereochemical behavior of the **9c** and **9d** the helimeric inversion barrier for these compounds was calculated using the quantum chemical methodology. The energy calculations reveal that the helimerization energy barriers for **9c** and **9d** are 20.26 and 18.53 kJ mol^{-1}, respectively. The calculated values of the inversion barrier of the helimeric enantiomers indicated a rapid interconversion at room temperature. The slightly higher energy barrier for **9c** as compared to **9d** is possibly due to the presence of the oxygen atom O2 in the seven membered ring **D** instead of sulfur. The presence of sulfur atom S2 in **9d** may provide better configurational flexibility as compared to **9c**.

The electronic absorption spectrum of **9c** recorded in THF solution displays bands at ~ 450, 300 and 250 nm. The observed electronic spectrum have been assigned with the help of time-dependent DFT (TD-DFT) calculations. Since each absorption line in a TD-DFT spectrum can arise from a several single orbital excitations, a description of the transition character is generally not straightforward. However, approximate assignments can be made, although they provide a simplified representation of the transitions. TD-DFT excitations were calculated both on the gas phase and in the solvent using the DCM (dichloromethane). By comparing the calculated spectra it is evident that calculated transitions do not exhibit significant solvatochromic effects. In this view, only the PCM model results are presented, Fig. 2 and 3.

The calculations reveal that the first lower energy band calculated at 462 nm arises due to the HOMO → LUMO transition *i.e.* from π → π*, however, as is apparent from the oscillator strength (*f*), the intensity is relatively weak, therefore this may be described as a local transition. The next two higher energy bands calculated at 306 and 256 nm, respectively, also arise from π → π* transitions without the involvement of the lone pair electrons of the sulfur atoms. The TD-DFT calculations for **9d** indicate that the nature of electronic transitions is similar to that of the **9c**. Similar calculations for compound **4f** indicate an electronic absorption band at 392 nm instead of ~460 nm observed for **9c**

Table 2 TD-DFT calculated excitation energies (E), oscillator strengths (f) and approximate assignments for **4f**, **9c** and **9d**

E/eV	λ/nm	f	Composition (%)	Approx. assign.
4f				
3.16	392	0.1933	HOMO → LUMO (44%)	π → π*, n → π*
3.88	319	0.2171	HOMO → LUMO (47%)	π → π*
4.94	251	0.4091	HOMO–1 → LUMO+1 (44%)	π → π*, n → π*
9c				
2.68	462	0.2228	HOMO → LUMO (48%)	π → π*
4.05	306	0.5445	HOMO-3 → LUMO (35%)	π → π*
4.84	256	0.1725	HOMO → LUMO+3 (45%)	π → π*
9d				
2.76	449	0.2019	HOMO → LUMO (49%)	π → π*
4.12	301	0.2845	HOMO–3 → LUMO (41%)	π → π*
4.78	259	0.1315	HOMO–3 → LUMO (29%)/ HOMO–2 → LUMO+2 (15%)	π → π*

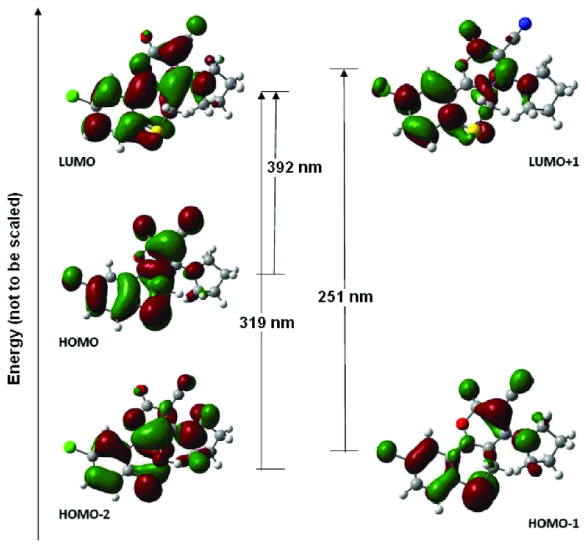


Fig. 2 Selected orbital excitations for **4f** (orbital contour value 0.03).

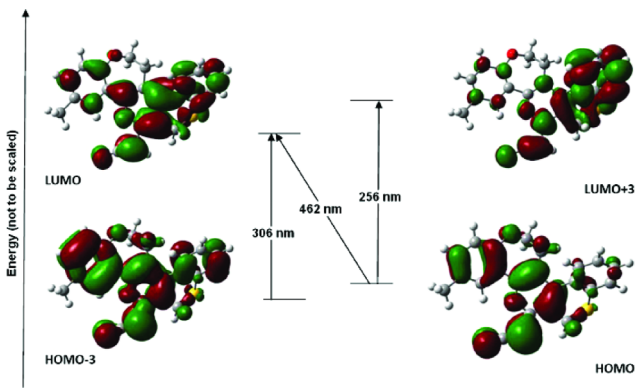


Fig. 3 Selected orbital excitations for **9c** (orbital contour value 0.03).

and **9d**. This relatively higher energy electronic absorption band is due to the involvement of the n → π* transition in addition to π → π* (Fig. 2 and 3). The calculated excitation energies and approximate assignments are presented in Table 2.

Conclusion

In conclusion, we have succeeded to develop an efficient non-catalytic route for the construction of partially reduced dioxathia- and oxadithiahelicenes through base-induced inter- and intramolecular C–C bond formation from the reaction of 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (**4**) with 3,4-dihydro-2*H*-benzo[*b*]oxepin-5(2*H*)-ones (**5a**), 3,4-dihydrobenzo[*b*]thiepin-5(2*H*)-one (**5b**) and thiochroman-4-ones (**2**) separately. We have studied the effect of partial reduction as well as the presence of hetero-atom on the helical parameters. These helical molecules have been obtained in only two steps in moderate yields. The synthetic strategy is so flexible that one can prepare a variety of heterohelicenes with more than two hetero-atoms in the outer helix with amino, nitrile and halo functionalities which can be further exploited for the ring construction and functional group transformation. The beauty of the synthetic protocol lies in obtaining partially reduced heterohelicenes without catalytic regioselective hydrogenation. The spatial distortion of backbone of the helicenes is influenced by helicity parameters such as bond lengths, dihedral angles and distance between terminal carbons and hydrogen atoms of the inner helix. The energy barriers are strongly dependent on the nature of hetero-atoms introduced in the heterohelicenes which is evidenced from the helicity parameters and configurational stability.

Experimental section

General

The reagents and the solvents used in this study were of analytical grade and were used without further purification. The melting points were determined on an electrically heated Townson Mercer melting point apparatus and are uncorrected. Commercial reagents were used without purification. ^{1}H and ^{13}C NMR spectra were measured on a Bruker WM-300 (300 MHz)/Jeol-400 using $CDCl_3$ and DMSO-d_6 as solvents. Chemical shifts are reported in parts per million shift (δ-value) from Me_4Si (δ 0 ppm for ^{1}H) or based on the middle peak of the solvent ($CDCl_3$) (δ 77.00 ppm for ^{13}C NMR) as the internal standard. Signal patterns are indicated as s, singlet; d, doublet; dd, double doublet; t, triplet; m, multiplet. Coupling constants (J) are given in Hertz.

Infrared (IR) spectra were recorded on a Perkin-Elmer AX-1 spectrophotometer in KBr disc and reported in wavenumbers (cm^{-1}). ESI-MS spectrometers were used for mass spectra analysis. ^{13}C NMR spectra of compounds **9** and **11** were not reported due to their very poor solubility in deuterated solvents such as $CDCl_3$ and DMSO-d_6 but their structure has also been assigned on the basis of X-ray diffraction of two representative compounds **9c** and **9d**.

General procedure for the synthesis of 4-(methylthio)-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (3)

A mixture of thiochroman-4-ones (5 mmol) **2** and methyl 2-cyano-3,3-dimethylthioacrylate **1** (5 mmol) in DMSO (8 mL) was stirred in the presence of powdered NaOH (7 mmol) for 14 h, at room temperature. The reaction mixture was poured onto crushed ice with vigorous stirring. The aqueous suspension was neutralized with 10% HCl and the precipitate obtained was filtered, washed with water, dried and crystallized from acetone.

4-(Methylthio)-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (3a). Canary yellow amorphous solid; yield 75%; mp 179–180 °C; IR (KBr): 2163 (CN), 1682 (C═O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 2.95 (s, 3H, CH_3), 4.06 (s, 2H, SCH_2), 7.36 (dd, 1H, J = 3.6 Hz, Ar-H), 7.47 (d, 2H, J = 3.6 Hz, Ar-H), 7.80 (d, 1H, J = 8.0 Hz, Ar-H) ppm; ^{13}C NMR (100 MHz, DMSO-d_6): δ 17.33, 23.10, 94.54, 109.17, 114.44, 125.43, 126.17, 127.20, 132.01, 135.97, 153.39, 156.82, 166.70 ppm; MS (CI): m/z = 287 (M^+), 277, 272, 203, 172, 136; HRMS (CI): calc. for $C_{14}H_9NO_2S_2$: 287.0075 (M^+); found: 287.0084.

9-Chloro-4-(methylthio)-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]-pyran-3-carbonitrile (3b). Canary yellow amorphous solid; yield 80%; mp 192–194 °C; IR (KBr): 2214 (CN), 1721 (C═O) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.94 (s, 3H, CH_3), 4.06 (s, 2H, SCH_2), 7.50 (m, 2H, Ar-H), 7.72 (m, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.79, 23.50, 95.41, 110.21, 114.79, 125.93, 127.33, 129.24, 130.95, 131.88, 135.36, 152.27, 157.02, 166.92 ppm; MS (CI): m/z = 321 (M^+), 308, 277.9, 245, 169.9; HRMS (ESI): calc. for $C_{14}H_8ClNO_2S_2$: 321.9763 (MH^+); found: 321.9777.

General procedure for the synthesis of 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles (4). A mixture of 4-(methylthio)-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles **3** (1 mmol) and *sec*-amine (1.1 mmol) was refluxed in absolute ethanol for 6 h. During this period a precipitate separated out which was filtered after cooling. The precipitate was washed with cold ethanol and finally crystallized with acetone.

2-Oxo-4-(pyrrolidin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (4a). Orange coloured crystalline solid; yield 63%; mp 230–232 °C; IR (KBr): 2197 (CN), 1715 (CO) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.91 (s, 4H, 2 × CH_2), 3.88 (s, 4H, 2 × NCH_2), 4.06 (s, 2H, SCH_2), 7.31–7.46 (m, 3H, Ar-H), 7.25 (d, 1H, J = 7.6 Hz, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.61 (2C), 26.24, 54.55 (2C), 71.41, 104.84, 118.83, 126.45, 126.82, 127.87 (2C), 131.80, 136.05, 154.33, 159.78, 161.73 ppm; MS(CI): m/z = 310 (M^+), 282, 242, 213, 187, 136; HRMS (CI): calc. for $C_{17}H_{14}N_2O_2S_2$: 310.0776 (M^+); found: 310.0772.

9-Chloro-4-morpholino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]-pyran-3-carbonitrile (4b). Orange coloured crystalline solid; yield 64%; mp 205–208 °C; IR (KBr): 2213 (CN), 1717 (C═O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 3.602 (t, 4H, J = 4.4 Hz, 2 × OCH_2), 3.786 (t, 4H, J = 4.4 Hz, 2 × NCH_2), 3.93 (s, 2H, SCH_2), 7.517 (d, 2H, J = 1.2 Hz, Ar-H), 7.714 (t, 1H, J = 1.2 Hz, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.21, 51.44, 65.86, 79.57, 79.95, 106.97, 116.14, 124.91, 128.26, 128.81, 130.96, 134.46, 154.44, 159.38, 164.38, 164.78 ppm; MS(CI): m/z = 360 (M^+), 332, 292, 274, 247, 169.9; HRMS (ESI): calc. for $C_{17}H_{13}ClN_2O_3S_2$: 361.0414 (MH^+); found: 361.0394.

2-Oxo-4-(piperidin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (4c). Orange coloured crystalline solid; yield 75%; mp 182–184 °C; IR (KBr): 2202 (CN), 1716 (C═O) cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.69 (br s, 6H, 3 × CH_2), 3.51 (m, 4H, 2 × NCH_2), 3.87 (s, 2H, SCH_2), 7.33 (m, 1H, Ar-H), 7.73 (m, 2H, Ar-H), 7.74 (d, 1H, J = 7.8 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.94, 24.72, 25.95 (2C), 52.72 (2C), 79.58, 106.76, 116.62, 126.01, 126.41, 127.22, 127.45, 131.70, 135.83, 155.90, 160.22, 165.51 ppm; MS(CI): m/z = 324 (M^+), 296, 256, 240, 213; HRMS (CI): calc. for $C_{18}H_{16}N_2O_2S$: 324.0932 (M^+); found: 324.0939.

4-Morpholino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (4d). Orange coloured crystalline solid; yield 79%; mp 216–218 °C; IR (KBr): 2212 (CN), 1714 (C═O) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 3.68 (m, 4H, 2 × OCH_2), 3.76 (m, 4H, 2 × NCH_2), 3.89 (s, 2H, SCH_2), 7.32 (m, 1H, Ar-H), 7.743 (m, 2H, Ar-H), 7.74 (d, 1H, J = 7.8 Hz, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.62, 51.78 (2C), 66.28 (2C), 79.99, 106.66, 116.65, 126.03, 126.45, 127.13, 127.47, 131.81, 135.85, 156.15, 160.06, 165.03 ppm; MS(CI): m/z = 326 (M^+), 298, 258, 240, 212; HRMS (CI): calc. for $C_{17}H_{14}N_2O_3S$: 326.0759 (M^+); found: 326.0756.

9-Chloro-2-oxo-4-(piperidin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (4e). Orange coloured crystalline solid; yield 57%; mp 240 °C; IR (KBr): 2211 (CN), 1712 (C═O) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 1.68 (br s, 6H, 3 × CH_2), 3.51 (br s, 4H, 2 × NCH_2), 3.89 (s, 2H, SCH_2), 7.49 (s, 2H, Ar-H), 7.79 (s, 1H, Ar-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.92, 24.75, 25.97 (2C), 52.80 (2C), 79.93, 107.46, 116.50, 125.29, 128.75, 129.18, 130.77, 131.25, 134.85, 154.63, 159.95, 165.24 ppm; MS(CI): m/z = 324 (M^+), 296, 256, 240, 213; HRMS (ESI): calc. for $C_{18}H_{15}ClN_2O_2S$: 359.0621 (M^+); found: 359.0619.

9-Chloro-2-oxo-4-(pyrrolidin-1-yl)-2,5-dihydrothiochromeno-[4,3-*b*]pyran-3-carbonitrile (4f). Orange coloured crystalline solid; yield 73%; mp 257–260 °C; IR (KBr): 2202 (CN), 1700 (C═O) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 1.92 (s, 4H, 2 × CH_2), 3.89 (s, 4H, 2 × NCH_2), 4.10 (s, 2H, SCH_2), 7.50 (s, 2H, Ar-H), 7.69 (s, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 25.13 (2C), 25.75, 54.16 (2C), 71.41, 105.05, 118.20, 125.27, 128.89, 129.15, 130.80, 130.91, 134.61, 154.45, 159.07, 161.03 ppm; MS (CI): m/z = 345 (M^+ + 1), HRMS (ESI): calc. for $C_{17}H_{13}ClN_2O_2S$: 345.0464 (MH^+); found: 345.0449.

9-Chloro-2-oxo-4-(4-phenylpiperazin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (4g). Canary yellow crystalline solid from DCM–methanol; yield 70%; mp 226–258 °C; IR (KBr): 2213 (CN), 1714 (CO) cm^{-1}; ^1H NMR (300 MHz, DMSO-d_6): δ 3.38 (s, 4H, 2 × NCH_2), 3.72 (s, 4H, 2 × NCH_2), 3.99 (s, 2H, SCH_2), 6.83 (t, 1H, J = 7.2 Hz, Ar-H), 7.00 (d, 2H, J = 8.1 Hz,

Ar-H), 7.25 (t, 2H, Ar-H), 7.53 (s, 2H, Ar-H), 7.73 (s, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.69, 48.72 (2C), 51.20 (2C), 80.59, 107.47, 115.90 (2C), 116.00, 119.54, 125.32, 128.69, 129.22 (2C), 130.80, 131.35, 134.91, 150.37, 154.33, 164.97 ppm; MS (ESI): m/z = 436 (M^+ + 1), HRMS (ESI): calc. for $C_{23}H_{18}N_3ClO_2S$: 436.0886 (MH^+); found: 436.0877.

2-Oxo-4-(4-phenylpiperazin-1-yl)-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (4h). Canary yellow amorphous solid; yield 69%; mp 206 °C; IR (KBr): 2228 (CN) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.5 (s, 4H, NCH_2), 3.72 (s, 4H, NCH_2), 3.96 (s, 2H, SCH_2), 6.83 (m, 1H, Ar-H), 7.01 (d, 2H, J = 7.8, Ar-H), 7.25 (t, 2H, J = 7.8, Ar-H), 7.34 (m, 1H, Ar-H), 7.44 (m, 2H, Ar-H), 7.76 (d, 1H, J = 7.8, Ar-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.71, 48.76 (2C), 51.16 (2C), 80.23, 106.76, 115.92 (2C), 116.67, 119.55, 126.07, 126.47, 127.17, 127.49, 129.06 (2C), 131.83, 135.91, 150.41, 156.15, 159.98, 165.23 ppm; MS (ESI): m/z = 402 (M^+ + 1), HRMS (ESI): calc. for $C_{23}H_{19}N_3O_2S$: 402.1276 (MH^+); found: 402.1270.

4-(4-Benzylpiperazin-1-yl)-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile (4i). Canary yellow crystalline solid from DCM–methanol; yield 76%; mp 196–198 °C; IR (KBr): 2206 (CN), 1714 (C═O) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.43 (s, 4H, 2 × NCH_2), 2.50 (s, 4H, 2 × NCH_2), 3.51 (s, 2H, SCH_2), 3.81 (s, 2H, CH_2), 7.21 (m, 1H, Ar-H), 7.26 (m, 5H, Ar-H), 7.34–7.38 (m, 2H, Ar-H), 7.68 (m, 1H, Ar-H) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ 24.90, 51.53 (2C), 52.71 (2C), 61.61, 89.75, 106.45, 115.55, 118.80, 119.80, 126.08, 126.49, 127.14, 127.50, 128.30 (2C), 128.92 (2C), 131.84, 135.71, 137.73, 147.35, 184.00 ppm; MS (ESI): m/z = 416 (M^+ + 1); HRMS (ESI): calc. for $C_{24}H_{21}N_3O_2S$: 416.1433 (MH^+); found: 416.1430.

Synthesis of 11-chloro-6,7-dihydro(bisthiochromeno[*b*,*e*])pyrano-[3,4-*c*]pyran-14,15-dione (8). A mixture of 4-(methylthio)-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitriles **3** (1 mmol) and 6-methylthiochroman-4-one (**2b**) and powdered KOH (1.2 mmol) in DMSO (3 mL) was stirred at room temperature for 14 h. After completion, reaction mixture was poured onto crushed ice with vigorous stirring and neutralized with 10% HCl. The crude product obtained was filtered off, washed with water and finally purified by silica gel column chromatography using 5–45% chloroform in hexane. Orange colored solid; yield 43%; mp 211–212 °C; IR (KBr): 1769 (C═O), 1670 (C═O) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.85 (s, 2H, SCH_2, merged in H_2O), 4.10 (s, 2H, SCH_2), 7.26–7.41 (m, 5H, Ar-H), 7.68 (m, 1H, Ar-H), 7.91 (m, 1H, Ar-H) ppm; HRMS (ESI): m/z calc. for $C_{22}H_{11}ClO_4S_2$: 437.9787 (M^+); found: 438.0001.

General procedure for the synthesis of (*Z*)-2-(1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-*d*]benzo[*b*]oxepine(2*H*)-ylidene)acetonitriles (9)

A mixture of 4-*sec*-amino-2-oxo-2,5-dihydrothiochromeno[4,3-*b*]pyran-3-carbonitrile **4** (1.0 mmol) and 3,4-dihydro-2*H*-benzo[*b*]oxepin/thiepin-5(2*H*)-one **5** (1 mmol) and powdered NaOH (1.2 mmol) in DMSO (3 mL) was stirred at room temperature for 14 h. After completion, reaction mixture was poured onto crushed ice with vigorous stirring and neutralized with 10% HCl. The crude product obtained was filtered off, washed with water and finally purified by silica gel column chromatography using 5–15% chloroform in hexane.

(*Z*)-2-(14-Chloro-4-methyl-1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-d]benzo[*b*]oxepine(2*H*)-ylidene)acetonitrile (9a). Red amorphous solid; yield 95%; mp 219–220 °C; UV($CHCl_3$), λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}): 286 nm (6625); 256 nm (10592); IR (KBr): 2142 (–CN) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.33 (s, 3H, CH_3), 2.72 (t, 2H, J = 6.0 Hz, CH_2), 3.60 (s, 2H, SCH_2), 4.42 (t, 2H, J = 6.0 Hz, OCH_2), 5.25 (s, 1H, CH), 7.02 (d, 1H, J = 9.0 Hz, Ar-H), 7.26 (d, 1H, J = 9.0 Hz, Ar-H), 7.43 (dd, 1H, J = 9.0 Hz and 3.0 Hz, Ar-H), 7.63 (m, 2H, Ar-H), 7.83 (s, 1H, Ar-H) ppm; MS: m/z = 405 (M^+), 406 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{23}H_{16}ClNO_2S$: 406.0669 (MH^+); found: 406.0662.

(*Z*)-2-(14-Chloro-4,6-dimethyl-1,2-dihydro-10*H*-thiochromeno-[3,4-*c*]pyrano[3,2-*d*]benzo[*b*]oxepine(2*H*)ylidene)acetonitrile (9b). Red amorphous solid; yield 58%; mp 184–186 °C; IR (KBr): 2191 (–CN) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.35 (s, 3H, CH_3), 2.49 (t, 2H, J = 6.3 Hz, CH_2), 2.54 (s, 3H, CH_3), 3.31 (s, 2H, SCH_2), 4.45 (s, 1H, CH), 4.58 (t, 2H, J = 6.3 Hz, OCH_2), 6.84 (s, 1H, Ar-H), 6.95 (s, 1H, Ar-H), 7.29 (d, 1H, J = 2.1 Hz, Ar-H), 7.41 (d, 1H, J = 1.8 Hz, Ar-H), 7.47 (m, 1H, Ar-H) ppm; MS: m/z = 420 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{24}H_{18}ClNO_2S$: 420.0825 (MH^+); found: 420.0822.

(*Z*)-2-(14-Chloro-6-methyl-1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-*d*]benzo[*b*]oxepine(2*H*)-ylidene)acetonitrile (9c). Red crystalline solid; yield 92%; mp 163–164 °C; IR (KBr): 2197 (–CN) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.30 (s, 3H, CH_3), 2.70 (br s, 2H, CH_2), 3.54 (s, 2H, SCH_2), 4.46 (br s, 2H, OCH_2), 5.23 (s, 1H, CH), 7.00 (m, 1H, Ar-H), 7.23 (m, 1H, Ar-H), 7.33 (m, 2H, Ar-H), 7.54 (m, 2H, Ar-H), 7.72 (m, 1H, Ar-H); MS: m/z = 372 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{23}H_{17}ClNO_2S$: 372.1058 (MH^+); found: 372.1041.

(*Z*)-2-(1,2-Dihydro-10*H*-thiochromeno[3,4-*c*]pyrano[3,2-*d*]-benzo[*b*]thiaoxepine(2*H*)-ylidene)acetonitrile (9d). Red amorphous solid; yield 40%; mp 142–144 °C; IR (KBr): 2196 (–CN) cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.44 (t, 2H, J = 6.6 Hz, CH_2), 3.32 (s, 2H, SCH_2), 3.66 (t, 2H, J = 6.6 Hz, SCH_2), 4.49 (s, 1H, CH), 7.29 (m, 2H, Ar-H), 7.39 (m, 1H, Ar-H), 7.53 (m, 3H, Ar-H), 7.69 (d, 1H, J = 7.2 Hz, Ar-H), 7.82 (d, 1H, J = 7.5 Hz, Ar-H) ppm; MS: m/z = 374 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{22}H_{15}NOS_2$: 374.0673 (MH^+); found: 374.0641.

(*Z*)-2-(14-Chloro-1,2-dihydro-10*H*-thiochromeno[3,4-*c*]pyrano-[3,2-*d*]benzo[*b*]thiaoxepine(2*H*)-ylidene)acetonitrile (9e). Red amorphous solid; yield 38%; mp 108–110 °C; IR (KBr): 2185 (–CN) cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.58 (br s, 2H, CH_2), 3.70 (br s, 2H, SCH_2), 3.93 (m, 2H, SCH_2), 4.57 (s, 1H, CH), 7.38 (m, 4H, Ar-H), 7.48 (m, 1H, Ar-H), 7.57 (m, 1H, Ar-H), 7.70 (m, 1H, Ar-H) ppm; MS: m/z = 408 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{22}H_{14}ClNOS_2$: 408.0284 (MH^+); found: 408.0279.

2-(5-Chloro-1*H*-dithiochromeno[4,3-*b*:4′,3′-*d*]pyran-14(7*H*)-ylidene)acetonitrile (11a). A mixture of **4g** (1.0 mmol), thiochroman-4-one **2** (1 mmol) and powdered KOH (1.2 mmol) in DMF (3 mL) was stirred at room temperature for 14 h. After completion, the reaction mixture was poured onto crushed ice with vigorous stirring and neutralized with 10% HCl. The crude product obtained was filtered off, washed with water and

finally purified by a silica gel column chromatography using 45% chloroform in hexane as an amorphous red solid; yield 25%; mp 218–220 °C; IR (KBr): 2191 (–CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.32 (s, 2H, SCH_2), 3.81 (s, 2H, SCH_2), 4.53 (s, 1H, CH), 7.32 (m, 6H, Ar-H), 7.50 (m, 1H, Ar-H) ppm; MS: m/z = 394 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{21}H_{12}ClNOS_2$: 394.0127 (MH^+); found: 394.0110.

2-(7,8-Dihydrobenzo[*f*]thiochromeno[4,3-*c*]isochromen-6(13*H*)-ylidene)acetonitrile (11b). Compound **11b** was prepared from the reaction of 5,6-dihydro-4-(4-methylpiperazin-1-yl)-2-oxobenzo[*h*]chromene-3-carbonitrile and thiochroman-4-one in the presence of powdered KOH. Usual work-up and crystallization from chloroform and hexane (3 : 1) gave red rod shaped crystals; yield 30%; mp 253–254 °C; IR (KBr): 2187 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (t, 2H, J = 7.2, Hz, CH_2), 2.82 (t, 2H, J = 7.2 Hz, CH_2), 3.98 (s, 2H, SCH_2), 4.46 (s, 1H, CH), 7.28–7.31 (m, 7H, Ar-H), 7.99 (m, 1H, Ar-H) ppm; MS: m/z = 342 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{22}H_{15}NOS$: 342.0953 (MH^+); found: 342.0951.

2-(3-Chloro-7,8-dihydrobenzo[*f*]thiochromeno[4,3-*c*]isochromen-6(13*H*)-ylidene)acetonitrile (11c). Compound **11c** was obtained from the reaction of 5,6-dihydro-4-(4-methylpiperazin-1-yl)-2-oxobenzo[*h*]chromene-3-carbonitrile and 6-chlorothiochroman-4-one and worked up as described above. red amorphous solid; yield 35%; mp 266–268 °C; IR (KBr): 2185 (CN) cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.35 (t, 2H, J = 7.2 Hz, CH_2), 2.82 (t, 2H, J = 7.2 Hz, CH_2), 3.98 (s, 2H, SCH_2), 4.50 (s, 1H, CH), 7.47 (m, 6H, Ar-H), 7.92 (s, 1H, Ar-H) ppm; MS: m/z = 376 (M^+ + 1); HRMS (ESI): m/z calc. for $C_{22}H_{14}ClNOS$: 376.0563 (MH^+); found: 376. 0545.

X-Ray diffraction studies

Intensity data for the colorless crystals of **4f**, **9c** and **9d** were collected at 132(2) K on a Bruker APEX-II CCD diffractometer system equipped with graphite-monochromated Mo-Kα radiation λ = 0.71073 Å. The final unit cell determination, scaling of the data and corrections for Lorentz and polarization effects were performed with Bruker SAINT.[30] Symmetry-related multiscan absorption corrections have been applied. In the case of **9d** no absorption correction was applied. The structures were solved by direct methods (SHELXS-97)[31] and refined by a full-matrix least-squares procedure based on F^2.[32] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were located at calculated positions and refined using a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq} value of the appropriate carrier atom. For **4f** the Flack's parameter was 0.48(6), which suggests that the solved structure is absolute. Figures for the compounds were prepared using ORTEP.[33] The relevant crystal and refinement parameters for the compounds **4f**, **9c** and **9d** (Fig. 1) are shown below.

Crystal data for 4f. $C_{17}H_{13}ClN_2O_2S$, M_r = 344.80, orthorhombic, space group $Pca2_1$, a = 8.7105(6), b = 8.3893(6), c = 41.097(3) Å, V = 3003.2(4) Å^3, Z = 8, D_c = 1.525 Mg m^{-3}, linear absorption coefficient 0.404 mm^{-1}, F(000) = 1424, crystal size 0.93 × 0.44 × 0.13 mm, reflections collected 54973, independent reflections 9542 [R_{int} = 0.1281], final indices [$I > 2\sigma(I)$]: R_1 = 0.0562, wR_2 = 0.1334; R indices (all data): R_1 = 0.0746, wR_2 = 0.1430, GOF = 1.038; largest difference peak and hole: 0.425 and –0.372 e Å^{-3}.

Crystal data for 9c. $C_{23}H_{17}NO_2S$, M_r = 371.44, monoclinic, space group $P2_1/n$, a = 7.723(2), b = 9.374(4), c = 24.947(7) Å, β = 95.26(3)°, V = 1798.5(10) Å^3, Z = 4, D_c = 1.372 Mg m^{-3}, linear absorption coefficient 0.198 mm^{-1}, F(000) = 776, crystal size 0.75 × 0.28 × 0.182 mm, reflections collected 21353, independent reflections 4276 [R_{int} = 0.0721], final indices [$I > 2\sigma(I)$]: R_1 = 0.0391, wR_2 = 0.1006; R indices (all data): R_1 = 0.0520, wR_2 = 0.1074, GOF = 1.020; largest difference peak and hole: 0.235 and –0.231 e Å^{-3}.

Crystal data for 9d. $C_{22}H_{15}NOS_2$, M_r = 373.47, monoclinic, space group $P2_1/c$, a = 11.8038, b = 16.2989(5), c = 19.3777(8) Å, β = 105.682(2)°, V = 3589.3(2) Å^3, Z = 8, D_c = 1.382 Mg m^{-3}, linear absorption coefficient 0.307 mm^{-1}, F(000) = 1552, crystal size 1.16 × 0.52 × 0.21 mm, reflections collected 48753, independent reflections 13628 [R_{int} = 0.1175], final indices [$I > 2\sigma(I)$]: R_1 = 0.0844, wR_2 = 0.1800; R indices (all data): R_1 = 0.1403, wR_2 = 0.2007, GOF = 1,176; largest difference peak and hole 0.759 and –0.518 e Å^{-3}.

Computational details

Density functional theory (DFT) calculations have been performed using the Gaussian 03 program.[34] The optimized ground and transition-state geometries were calculated using the B3LYP exchange–correlation functional[35] and using GDIIS[36] algorithm. The triple zeta 6-311+G* basis set for all atoms and tight SCF convergence criteria were used for the geometry optimization. For ground state optimization, wave function stability calculations were performed to confirm that the calculated wave functions corresponded to the ground state. The presence of one negative frequency was observed in the case of the transition-state geometries. The optimized ground state structures of the compounds were used for molecular orbital analyses and time-dependent DFT (TD-DFT) calculations at the B3LYP/6-311G** level of theory with the polarized continuum model (PCM).[37] The solvent parameters were those of the tetrahydrofuran. The energies and intensities of the 30 lowest energy spin-allowed electronic excitations were calculated using TD-DFT.

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