Reactions of 2-(Diformylmethylidene)-3,3-dimethylindole with Hydrazides: Synthesis of New Pyrazolylindolenine Derivatives—The Unprecedented One-Pot Pyrazole–Thiadiazole Double Annulation

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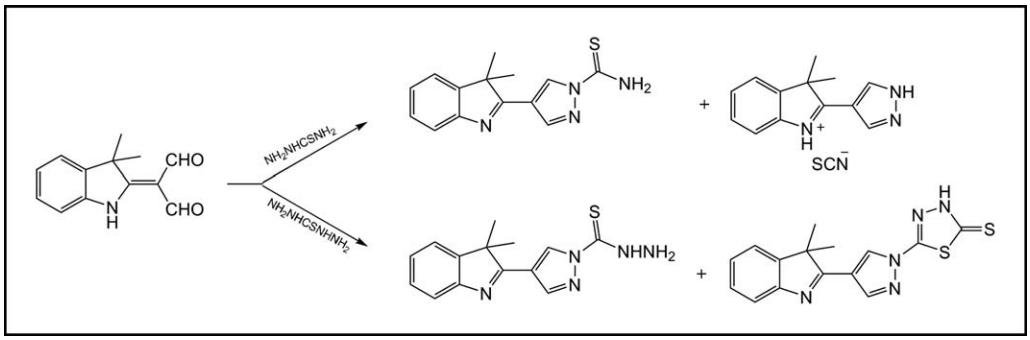

A series of new pyrazolylindolenine derivatives has been synthesized through the reaction of 2-(diformylmethylidene)-3,3-dimethylindole (diformyl), prepared by the Vilsmeier reaction, with six different hydrazides. Although the reaction of *p*-toluenesulfonylhydrazide and S-benzyldithiocarbazide with diformyl yielded the expected pyrazolylindolenines as the sole products, the initial products of the reactions of diformyl with semicarbazide, thiosemicarbazide, and carbohydrazide underwent cleavage. The reaction of diformyl with thiocarbohydrazide resulted in a unique one-pot formation of pyrazole and thiadiazole rings, conjugated with the indolenine component. The solid state structures of these heterocycles were established by X-ray crystallographic analysis.

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INTRODUCTION

Pyrazole derivatives constitute an important class of therapeutic agents in medicinal chemistry owing to their effectiveness as antitumor [1], anti-inflammatory [2], antihypertensive [3], antipsychotic [4], and neuroprotective [5] agents. Among the several syntheses of pyrazoles, which have been developed so far, one of the most common methods involves the reaction of 1,3-dicarbonyls with hydrazine derivatives [6]. The reaction proceeds by the initial formation of the monohydrazones that are then converted to the pyrazoles by the action of heat or acids.

Some years ago, Baradarani and coworkers described the reaction of 2,3,3-trimethylindolenine with the Vilsmeier reagent to produce aminomethylene-malondialdehyde **1** (Fig. 1) [7]. Later work by the same group [8] showed that this 2-(diformylmethylidene)-3,3-dimethylindole (diformyl) compound can react with arylhydrazines at room temperature to generate monohydrazones **2a** or **2b** as pure products, although it was not possible to ascertain which carbonyl group had reacted. Furthermore, it was reported that heating the hydrazones in refluxing ethanol gave rise to 4-(3,3-dimethylindol-2-yl)-substituted pyrazoles **3**, with migration of the double bond into the dihydropyrrole ring (Scheme 1). We have now been able to determine the structure of the reported monohydrazone **2**. Moreover, we report the result of our investigation on the reaction of the diformyl **1** with hydrazides. Crystal structures of the synthesized compounds were also determined using single-crystal X-ray diffraction data.

RESULTS AND DISCUSSION

The ^{1}H NMR spectrum of the monohydrazone obtained from the reaction of the diformyl and phenylhydrazine shows the gem-dimethyl hydrogens at δ 1.72 ppm, the imine hydrogen at δ 8.30 ppm, and the aldehyde hydrogen at δ 10.00 ppm. To elucidate the structure of the compound, we have examined the possible NOE correlations between these hydrogens. The compound shows no NOE effect between the gem-methyl

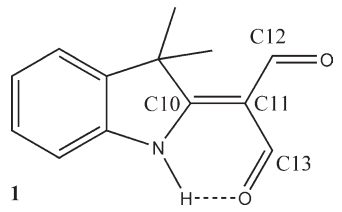

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Figure 1. 2-(Diformylmethylidene)-3,3-dimethylindole (**1**).

hydrogens and the imine hydrogen, whereas the effect was observed between the aldehyde and the methyl hydrogens. Therefore, the structure of the monohydrazone is unambiguously **2b**. This was further established by X-ray crystallographic analysis. Figure 2a shows the solid state structure of **2b** in which the imine link adopts the *trans* configuration stabilized by NH···N hydrogen bonding. The greater reactivity of the C(13) in the diformyl **1** in comparison with C(12) may be because of the Bürgi–Dunitz direction of approach of the hydrazine, which would be blocked by the gem-dimethyl group if nucleophilic attack took place at the C12 [9]. Attack at the C13, activated by intramolecular H-bonding, takes place away from the geminal methyl groups.

The hydrazone was then converted to pyrazolylindolenine **3** by heating. The X-ray crystal structure of **3** shows that the indolenine and the pyrazole components are nearly coplanar, attesting to conjugation between these two heterocycles. This system and the third aromatic ring, *i.e.*, the phenyl group are not coplanar (Fig. 2b). The selected bond distances and bond angels of **2b** and **3** are given in Table 1. To explore further aspects of the chemistry of this polyfunctional compound, we studied the reactions of the diformyl **1** with different hydrazides (Scheme 2).

The reaction of *p*-toluenesulfonylhydrazide was carried out in refluxing ethanol in the presence of acetic acid to give compound **4** as the only product. Under the same conditions S-benzyldithiocarbazide [10] reacted efficiently with the diformyl **1** to give the pyrazole **5**. It is noteworthy that neither the *p*-toluenesulfonyl nor the S-benzyldithiocarbonyl groups were cleaved under the applied conditions.

Diformyl **1** reacted with semicarbazide hydrochloride in ethanol at room temperature to form the 1-carbamoylpyrazole **6**. However, conducting the reaction in refluxing ethanol resulted in loss of the carbamoyl group, leading to the indoleninium chloride salt **7**. Similarly, the reaction of thiosemicarbazide with diformyl **1** afforded the 1-thiocarbamoylpyrazole **8** and (after loss of the thiocarbamoyl group) the indoleninium thiocyanate salt **9**, as a mixture. Our attempts to prevent the loss of the thiocarbamoyl moiety were unsuccessful; however, the pure products were easily obtained by sequential crystallization. 1-(Thio)carbamoylpyrazole derivatives are an intriguing class of chelating ligands and important intermediates in synthesizing a

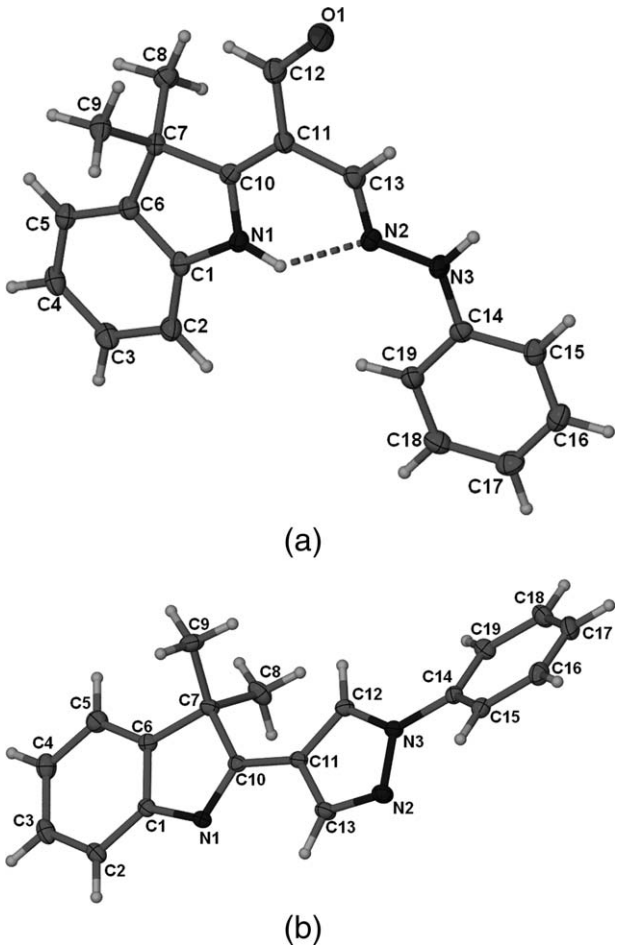


Figure 2. The crystal structure of compounds (a) **2b** and (b) **3** .

Scheme 1

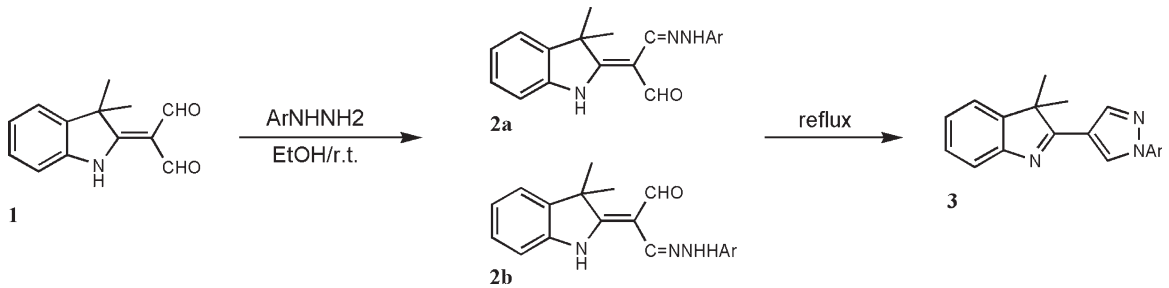
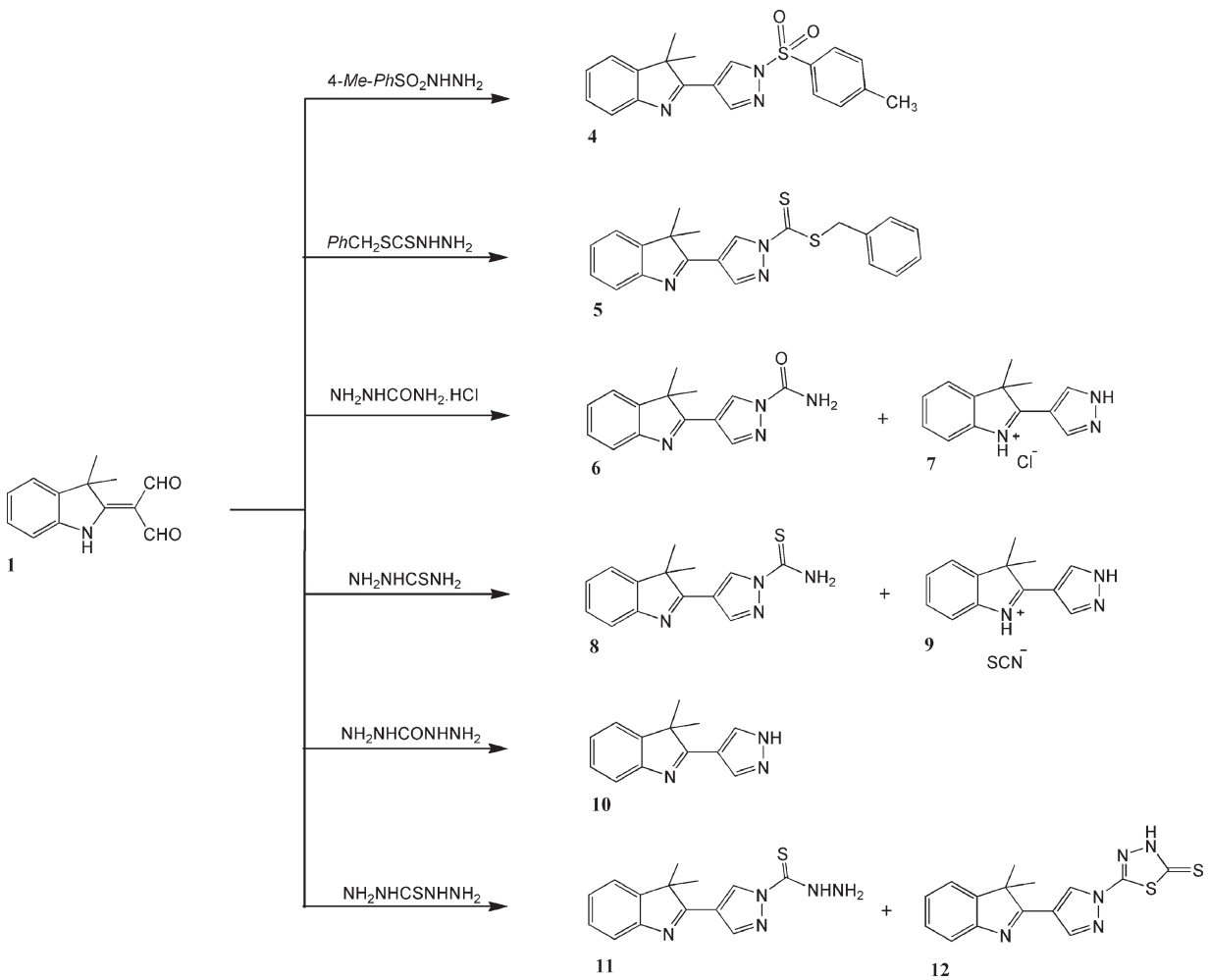


Table 1

Selected bond lengths and bond angles for compounds **2b** and **3**.

Compound **2b**		Compound **3**	
Bond lengths (Å)			
O(1)—C(12)	1.2344(19)	N(1)—C(10)	1.2995(16)
N(1)—C(10)	1.344(2)	N(1)—C(1)	1.4189(17)
N(1)—C(1)	1.402(2)	N(2)—C(13)	1.3158(18)
N(2)—C(13)	1.288(2)	N(2)—N(3)	1.3606(15)
N(2)—N(3)	1.3652(19)	N(3)—C(12)	1.3437(16)
N(3)—C(14)	1.387(2)	N(3)—C(14)	1.4261(17)
C(10)—C(11)	1.391(2)	C(10)—C(11)	1.4503(19)
C(11)—C(12)	1.430(2)	C(11)—C(12)	1.3751(18)
C(11)—C(13)	1.452(2)	C(11)—C(13)	1.4010(19)
Bond angles (°)			
C(13)—N(2)—N(3)	117.29(13)	N(2)—N(3)—C(14)	119.49(11)
N(2)—N(3)—C(14)	119.07(13)	C(9)—C(7)—C(8)	111.58(12)
C(9)—C(7)—C(8)	110.85(13)	N(1)—C(10)—C(11)	120.38(12)
N(1)—C(10)—C(11)	120.94(14)		
C(12)—C(11)—C(13)	116.51(14)		
O(1)—C(12)—C(11)	125.64(16)		
N(2)—C(13)—C(11)	122.85(14)		

Scheme 2



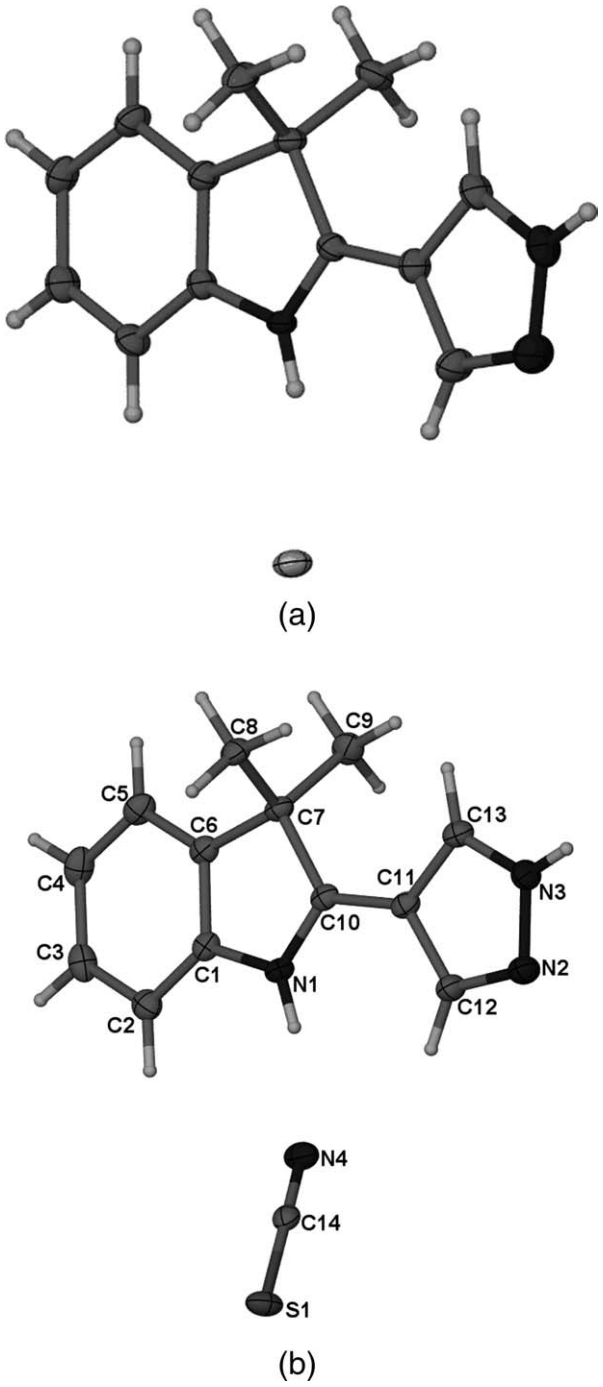


Figure 3. The crystal structure of compounds (a) **7** and (b) **9**.

variety of heterocyclic compounds [11]. It is well known that the (thio)carbamoyl group tends to cleave on heating or by the action of bases. In fact, this cleavage can lead to an interesting series of metal complexes in coordination chemistry [12]. Evidently, the indolenine nitrogen of compounds **6** and **8** acts as a base and is then converted to the related indoleninium salts, facilitating the cleavage of the (thio)carbamoyl group. The X-ray crystal structures of **7** and **9** confirm the formation of indoleninium salts (Fig. 3). The selected interatomic distances and bond angels for compound **9** are listed in Table 2.

Table 2

Selected bond lengths and bond angles for compound **9**.

Bond lengths (Å)	
S(1)—C(14)	1.648(2)
N(1)—C(10)	1.300(2)
N(2)—C(13)	1.324(2)
N(2)—N(3)	1.370(2)
N(3)—C(12)	1.321(2)
N(4)—C(14)	1.162(2)
C(10)—C(11)	1.427(3)
C(11)—C(12)	1.398(3)
C(11)—C(13)	1.420(3)
Bond angles (°)	
C(9)—C(7)—C(8)	110.26(15)
N(1)—C(10)—C(11)	122.14(17)
N(4)—C(14)—S(1)	178.79(17)

Finally, the reactions of the dialdehyde with carbohydrazide and thiocarbohydrazide were investigated. Regardless of the experimental conditions, the only product obtained from the reaction with carbohydrazide was (1*H*-pyrazole-4-yl)-3*H*-indole **10**, which was also obtained from the reaction of hydrazine and the diformyl [8]. It would appear that the first formed intermediate is very unstable and immediately decomposes to compound **10**. The reaction of the dialdehyde with thiocarbohydrazide led to the formation of the pyrazole-*N*-thiocarbohydrazide **11** and the thiadiazole-2-thione **12**. To the best of our knowledge, this protocol for formation of thiadiazole ring is unprecedented as is the arrangement of heterocyclic systems, *i.e.*, pyrazole-*N*-yl-1,3,4-thiadiazole-2-thione. Although thiadiazole-2-thione fused to the C atom of pyrazoles is known [13], analogous fusion to the N atom of pyrazoles is not. The crystal structure of compounds **11** and **12** are depicted in Figure 4 and selected bond lengths and bond angles are given in Table 3. The structure of **12** shows the three heterocyclic rings as coplanar, indicating conjugation between them, in contrast to compound **3**. This presumption is supported by the shorter bond length of N(3)—C(14) in **12** (1.39 Å) compared with the one in **3** (1.43 Å), attesting its significant double bond character.

The reaction mechanism for the formation of pyrazolylindolenine **11** is fundamentally the same as that for the formation of the other pyrazolylindolenines. To account for the formation of compound **12** two possible mechanisms were considered (Scheme 3). One involves intermolecular reaction of two molecules of compound **11** (*i*) [14]. The second alternative requires the nucleophilic attack of a second molecule of thiocarbohydrazide on compound **11** (*ii*). The intermediate then undergoes cyclocondensation to form the five membered ring of 1,3,4-thiadiazole. The first mechanism may be ruled out, as it would lead to formation of pyrazolylindolenine **10** that was not detected under the

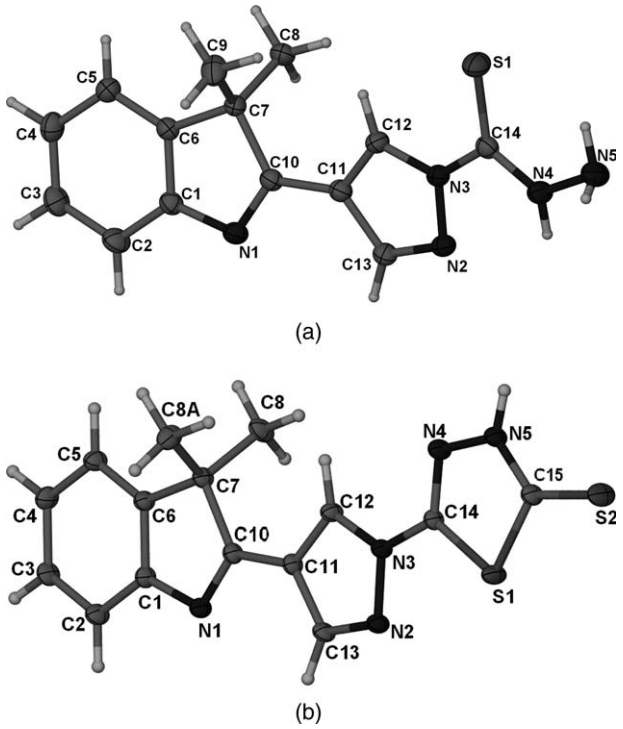


Figure 4. The crystal structure of compounds (a) **11** and (b) **12**.

reaction conditions. Moreover, refluxing an ethanolic solution of pyrazole-*N*-thiocarbohydrazide **11** in the presence of acetic acid did not give compound **12**. In the light of the above, path (*ii*) is the preferred mechanism of the reaction.

It is significant that although the synthesis of pyrazoles using benzoic hydrazide and analogues has been reported [11e,15], our attempts to react benzoic hydrazide with the dialdehyde **1** under different conditions were unsuccessful. In fact, the only product obtained was 1,2-dibenzoylhydrazine [16], the product of transacylation of benzoic hydrazide.

EXPERIMENTAL

Melting points were determined using a MEL-TEMP II melting point instrument and were not corrected. Microanalyses were carried out on a PerkinElmer 2400 elemental analyzer. ^{1}H NMR and ^{13}C NMR spectra were determined with a JEOL Lambda 400 MHz FT NMR (^{1}H: 400 MHz and ^{13}C: 100.4 MHz) spectrometer. Chemical shifts are given in δ values (ppm) using TMS as the internal standard. The IR spectra were taken with a PerkinElmer RX1 FTIR spectrophotometer. The mass spectra were taken on an Agilent 1200 LC/MS. X-ray diffraction data were collected on a Bruker APEX II CCD diffractometer using Mo Kα radiation. The structures were solved by direct methods and refined by a full-matrix least-squares procedure based on F^2.

Reaction with *p*-toluenesulfonylhydrazide. A solution of the dialdehyde (**1**; 0.43 g, 2 mmol) and *p*-toluenesulfonylhydrazide (0.372 g, 2 mmol) in ethanol (20 mL) in the presence of acetic acid (0.2 mL) was refluxed for 4 h. The solution was evaporated to half of its volume and then set aside at room temperature overnight, whereupon pale yellow crystals of the compound **4** were obtained.

3,3-Dimethyl-2-[1-(p-toluenesulfonyl)-1H-pyrazol-4-yl]-3H-indole (4). Yield: 0.65 g, 89%. mp 160–162°C; IR (KBr, cm^{-1}): 2961, 1594, 1575, 1454, 1377, 1324, 1180, 1094,1075, 673, 585; ^{1}H NMR (DMSO-d_6): δ 1.43 (s, 6H, gem-CH_3), 2.39 (s, 3H, Ar-CH_3), 7.25 (m, 1H, Ar-H), 7.32 (m, 1H, Ar-

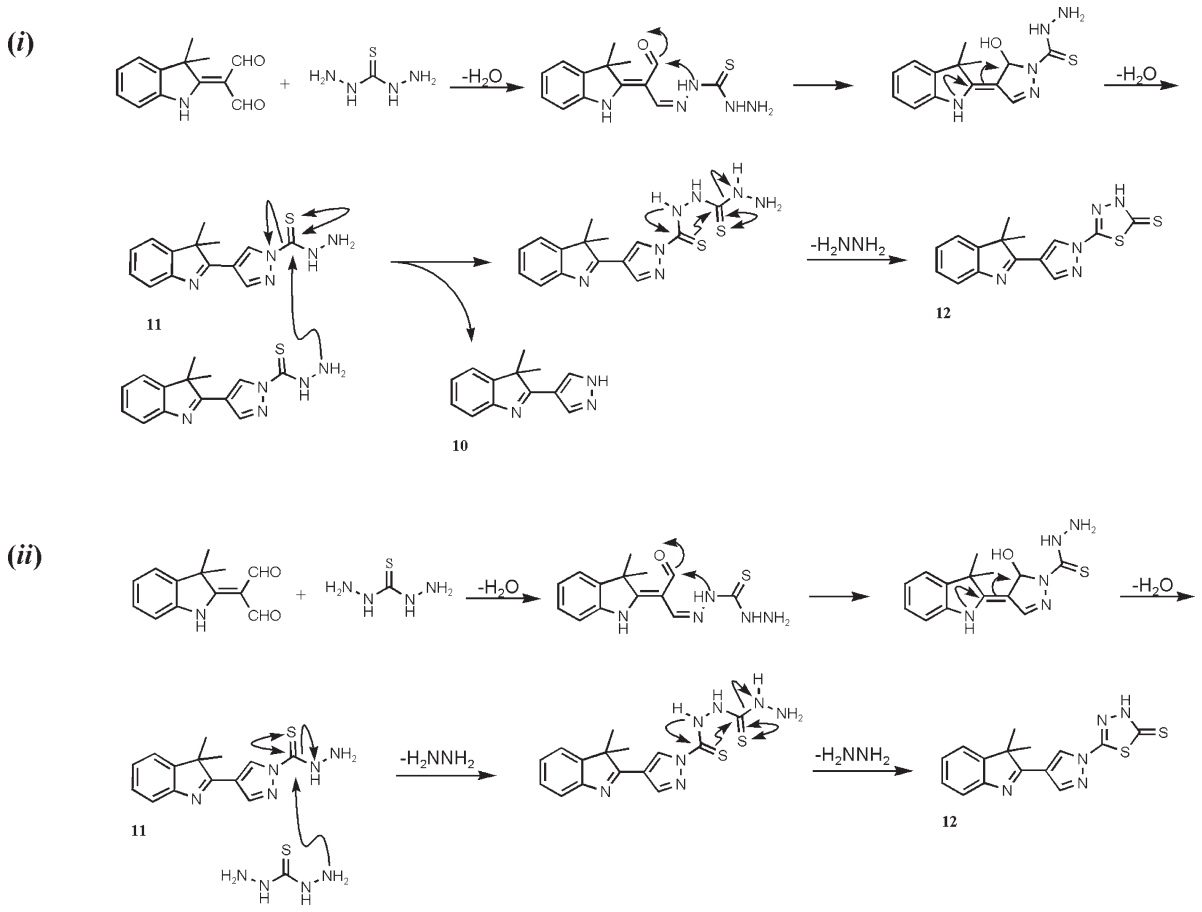
Table 3

Selected bond lengths and bond angles for compounds **11** and **12**.

Compound **11**		Compound **12**	
Bond lengths (Å)			
S(1)—C(14)	1.6522(17)	S(1)—C(14)	1.722(3)
N(1)—C(10)	1.297(2)	S(1)—C(15)	1.751(3)
N(1)—C(1)	1.424(2)	S(2)—C(15)	1.657(3)
N(2)—C(13)	1.316(2)	N(5)—C(15)	1.338(3)
N(2)—N(3)	1.3729(19)	N(5)—N(4)	1.376(3)
N(3)—C(12)	1.351(2)	N(3)—C(12)	1.353(3)
N(3)—C(14)	1.410(2)	N(3)—N(2)	1.370(3)
N(4)—C(14)	1.313(2)	N(3)—C(14)	1.387(3)
N(4)—N(5)	1.414(2)	N(2)—C(13)	1.320(3)
C(10)—C(11)	1.450(2)	N(1)—C(10)	1.300(3)
C(11)—C(12)	1.366(2)	C(12)—C(11)	1.373(4)
C(11)—C(13)	1.425(2)	C(11)—C(13)	1.419(4)
		C(11)—C(10)	1.456(3)
Bond angles (°)			
N(2)—N(3)—C(14)	122.07(13)	N(2)—N(3)—C(14)	119.1(2)
C(14)—N(4)—N(5)	122.15(16)	S(2)—C(15)—S(1)	124.15(16)
C(8)—C(7)—C(9)	110.99(16)	N(1)—C(10)—C(11)	122.0(2)
N(1)—C(10)—C(11)	121.97(15)	C(8)—C(7)—C(8)#1	111.0(2)
C(13)—C(11)—C(10)	128.72(16)		
N(4)—C(14)—S(1)	125.03(14)		

Symmetry transformations used to generate equivalent atoms: #1 $x,-y+1/2,z$.

Scheme 3



H), 7.50–7.55 (m, 4H, Ar-H), 8.00 (d, 2H, J = 8.4 Hz, Ar-H), 8.49 (s, 1H, pyrazolyl-H), 9.11 (s, 1H, pyrazolyl-H); ^{13}C NMR (DMSO-d_6): δ 21.16, 23.39, 52.90, 118.38, 120.08, 121.48, 125.73, 127.67, 128.05, 130.50, 131.06, 132.86, 144.75, 146.68, 146.78, 152.98, 176.68; MS: m/z 366 (MH^+); Anal. Calcd for $C_{20}H_{19}N_3O_2S$: C, 65.73; H, 5.24; N, 11.50; O, 8.76; S, 8.77%. Found: C, 65.60; H, 5.24; N, 11.29; S, 8.69%.

Reaction with S-benzyldithiocarbazate. A solution of the dialdehyde (**1**; 0.43 g, 2 mmol) and S-benzyldithiocarbazate [10] (0.396 g, 2 mmol) in ethanol (30 mL) in the presence of acetic acid (1 mL) was refluxed for 3 h and then cooled at room temperature. Compound **5** was separated as a yellow solid on addition of water (30 mL) to the solution. It was collected and washed with cold ethanol and dried over silica gel. The crystal for X-ray analysis was obtained by slow evaporation of an ethanolic solution at room temperature.

4-(3,3-Dimethyl-3H-indol-2-yl)-pyrazole-1-carbodithioic acid benzyl ester (5). Yield: 0.52 g, 68%. mp 143–144°C; IR (KBr, cm^{-1}): 3141, 2968, 1578, 1373, 1169, 1073, 843, 755; ^{1}H NMR (DMSO-d_6): δ 1.45 (s, 6H, CH_3), 4.61 (s, 2H, CH_2), 7.25–7.37 (m, 5H, Ar-H), 7.46 (d, 2H, J = 7.2 Hz, Ar-H), 7.52 (d, 1H, J = 7.2 Hz, Ar-H), 7.58 (d, 1H, J = 7.6 Hz, Ar-H), 8.66 (s, 1H, pyrazolyl-H), 9.17 (s, 1H, pyrazolyl-H); ^{13}C NMR (DMSO-d_6): δ 23.52, 40.32, 52.90, 119.86, 120.27, 121.56, 125.97, 127.74, 127.79, 128.59, 128.62, 129.39, 134.66, 144.95, 146.82, 153.07, 176.56, 199.13; MS: m/z 378 (MH^+); Anal. Calcd for $C_{21}H_{19}N_3S_2$: C, 66.81; H, 5.07; N, 11.13; S, 16.99%. Found: C, 66.07; H, 5.21; N, 10.96; S, 16.77%.

Reaction with semicarbazide hydrochloride. A solution of the dialdehyde (**1**; 0.43 g, 2 mmol) and semicarbazide hydrochloride (0.223 g, 2 mmol) was stirred in ethanol (15 mL) at room temperature for 1 day during which compound **6** precipitated as a pale yellow solid. The solid was filtered, washed with $NaHCO_3$ aqueous solution and cold ethanol and dried over silica gel. More solid was obtained from the filtrate. Suitable crystal for X-ray analysis was grown in EtOAc. Compound **7** was obtained as colorless crystals by conducting the reaction in refluxing ethanol for 5 h and leaving the solution at room temperature for 2 days.

4-(3,3-Dimethyl-3H-indol-2-yl)-pyrazole-1-carboxamide (6). Yield: 0.36 g, 71%. mp 176–178°C; IR (KBr, cm^{-1}): 3383, 3237, 2973, 1741, 1570, 1441, 1356, 1207, 965, 753; ^{1}H NMR (DMSO-d_6): δ 1.57 (s, 6H, CH_3), 7.37 (m, 1H, indolenine-H), 7.43 (m, 1H, indolenine-H), 7.62–7.65 (m, 2H, indolenine-H), 8.18 (s, 1H, NH_2), 8.23 (s, 1H, NH_2), 8.68 (s, 1H, pyrazolyl-H), 9.23 (s, 1H, pyrazolyl-H); ^{13}C NMR (DMSO-d_6): 24.03, 52.98, 114.08, 117.53, 122.48, 127.23, 128.44, 132.22, 142.75, 144.65, 145.29, 149.16, 178.47; MS: m/z 255 (MH^+); Anal. Calcd for $C_{14}H_{14}N_4O$: C, 66.13; H, 5.55; N, 22.03; O, 6.29%. Found: C, 66.02; H, 5.69; N, 21.94%.

3,3-Dimethyl-2-(1H-pyrazol-4-yl)-3H-indolium chloride (7). Yield: 0.37 g, 75%. mp 266–268°C; IR (KBr, cm^{-1}): 3084, 1611, 1593, 1244, 1154, 762; ^1H NMR (DMSO-d_6): δ 1.68 (s, 6H, CH_3), 7.44–7.53 (m, 2H, indolenine-H), 7.66 (d, 1H, $J = 7.6$ Hz, indolenine-H), 7.76 (d, 1H, $J = 7.2$ Hz, indolenine-H), 9.06 (s, 2H, pyrazolyl-H); ^{13}C NMR (DMSO-d_6): δ 23.94, 52.57, 109.38, 115.56, 122.93, 127.46, 128.73, 138.52, 141.01, 142.86, 179.64; Anal. Calcd for $C_{13}H_{14}ClN_3$: C, 63.03; H, 5.70; N, 16.96%. Found: C, 62.90; H, 5.89; N, 16.81%.

Reaction with thiosemicarbazide. A solution of the dialdehyde (**1**; 0.43 g, 2 mmol) and thiosemicarbazide (0.182 g, 2 mmol) in ethanol (20 mL) in the presence of acetic acid (0.5 mL) refluxed for 1 h. The solvent was evaporated, and the resulting solid was dissolved in EtOAc:Hexane (7:3) and set aside at room temperature. In a few hours, the yellow crystals of the compound **9** were obtained. The crystals were collected, and the solution was set aside for 1 day, whereupon the yellow crystals of compound **8** were separated out.

4-(3,3-Dimethyl-3H-indol-2-yl)-pyrazole-1-carbothioamide (8). Yield: 0.34 g, 63%. mp 152–154°C; IR (KBr, cm^{-1}): 3377, 3256, 2964, 1621, 1576, 1455, 1370, 1186, 1100, 974, 872, 757, 632; ^1H NMR (DMSO-d_6): δ 1.44 (s, 6H, CH_3), 7.25 (m, 1H, indolenine-H), 7.34 (m, 1H, indolenine-H), 7.52 (d, 1H, $J = 7.2$ Hz, indolenine-H), 7.56 (d, 1H, $J = 7.6$ Hz, indolenine-H), 8.52 (s, 1H, pyrazolyl-H), 9.15 (s, 1H, pyrazolyl-H), 9.72 (s, 1H, NH_2), 10.20 (s, 1H, NH_2); ^{13}C NMR ($CDCl_3$): δ 24.51, 53.30, 119.86, 120.67, 121.06, 125.98, 127.98, 130.17, 143.57, 146.40, 153.39, 176.81, 177.69; MS: *m/z* 271 (MH^+); Anal. Calcd for $C_{14}H_{14}N_4S$: C, 62.20; H, 5.22; N, 20.72; S, 11.86%. Found: C, 61.86; H, 5.08; N, 20.49; S, 11.71%.

3,3-Dimethyl-2-(1H-pyrazol-4-yl)-3H-indolium thiocyanate (9). Yield: 0.15 g, 28%. mp 177–180°C; IR (KBr, cm^{-1}): 3105, 2078, 1610, 1594, 1249, 1163, 944, 761; ^1H NMR (DMSO-d_6): δ 1.65 (s, 6H, CH_3), 7.39–7.50 (m, 2H, indolenine-H), 7.58 (d, 1H, $J = 7.3$ Hz, indolenine-H), 7.74 (d, 1H, $J = 7.3$ Hz, indolenine-H), 8.85 (s, 2H, pyrazolyl-H); ^{13}C NMR (DMSO-d_6): δ 25.49, 53.24, 110.14, 116.28, 123.50, 128.02, 129.35, 138.64, 141.96, 143.52, 180.75, 206.72; Anal. Calcd for $C_{14}H_{14}N_4S$: C, 62.20; H, 5.22; N, 20.72; S, 11.86%. Found: C, 61.91; H, 5.41; N, 20.42; S, 11.60%.

Reaction with thiocarbohydrazide. A mixture of the dialdehyde (**1**; 0.43 g, 2 mmol) and thiocarbohydrazide (0.318 g, 3 mmol) in ethanol (20 mL) in the presence of acetic acid (0.5 mL) was refluxed for 4 h during which the compound **12** precipitated out. It was filtered, washed with water and ethanol, and dried over silica gel. A Suitable crystal for X-ray analysis was obtained by recrystallization from DMSO. Compound **11** was separated out as a yellow solid on addition of water to the filtrate and recrystallized from ethyl acetate to give the X-ray quality crystals.

4-(3,3-Dimethyl-3H-indol-2-yl)-pyrazole-1-carbothioic acid hydrazide (11). Yield: 0.31 g, 54%. mp 149–150°C; IR (KBr, cm^{-1}): 3260, 2965, 1579, 1540, 1454, 1358, 1246, 1165, 1014, 896, 750; ^1H NMR ($CDCl_3$): δ 1.52 (s, 6H, CH_3), 4.76 (bs, 2H, NH_2), 7.25–7.39 (m, 3H, indolenine-H), 7.66 (d, 1H, J =7.2 Hz, indolenine-H), 8.40 (s, 1H, pyrazolyl-H), 9.05 (s, 1H, pyrazolyl-H), 9.97 (bs, 1H, NH); ^{13}C NMR ($CDCl_3$): δ 24.56, 53.31, 118.98, 120.67, 121.07, 125.95, 128.01, 130.26, 143.19, 146.38, 153.49, 174.79, 176.90; MS: *m/z* 286 (MH^+); Anal. Calcd for $C_{14}H_{15}N_5S$: C, 58.92; H, 5.30; N, 24.54; S, 11.24%. Found: C, 58.49; H, 5.58; N, 24.23; S, 11.09%.

5-[4-(3,3-Dimethyl-3H-indol-2-yl)-pyrazol-1-yl]-3H-[1,3,4]thiadiazole-2-thione (12). Yield: 0.09 g, 14%. mp 312–314°C; IR (KBr, cm^{-1}): 3076, 2965, 1583, 1431, 1257, 1192, 1059, 739; ^1H NMR (DMSO-d_6): δ 1.48 (s, 6H, CH_3), 7.27 (m, 1H, indolenine-H), 7.35 (m, 1H, indolenine-H), 7.53 (d, 1H, $J = 6.8$ Hz, indolenine-H), 7.58 (d, 1H, $J = 7.2$ Hz, indolenine-H), 8.58 (s, 1H, pyrazolyl-H), 9.14 (s, 1H, pyrazolyl-H), 10.58 (s, 1H, NH); ^{13}C NMR (DMSO-d_6): δ 23.43, 52.91, 119.14, 120.07, 121.52, 125.73, 127.48, 127.72, 143.59, 146.82, 152.95, 153.08, 176.86, 186.17; Anal. Calcd for $C_{15}H_{13}N_5S_2$: C, 55.02; H, 4.00; N, 21.39; S, 19.59%. Found: C, 54.77; H, 3.84; N, 21.75; S, 19.36%.

SUPPLEMENTARY DATA

Crystallography data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC. 764076–764085.

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