Synthesis and characterisation of some novel indeno[1,2-*c*]pyrazoles

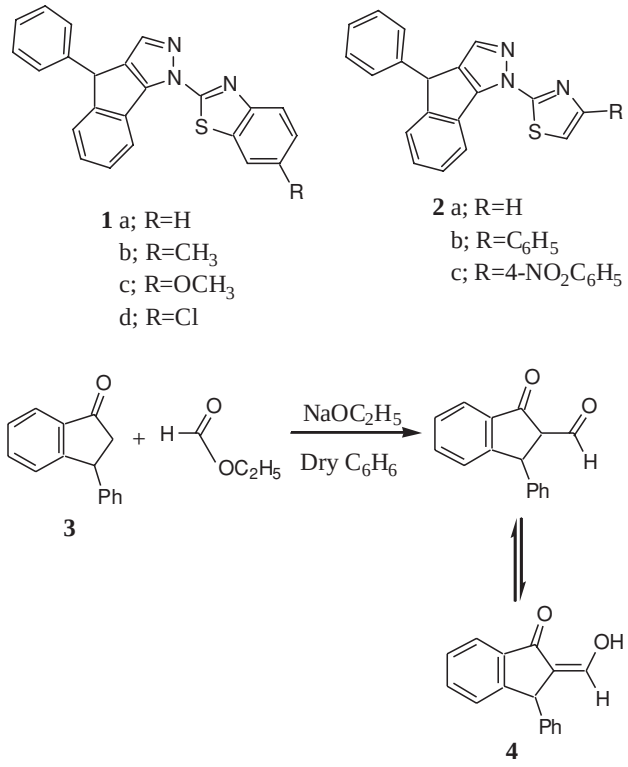
Karan Singh*, Pawan K. Sharma, S. N. Dhawan and Shiv P. Singh

Department of Chemistry, Kurukshetra University, Kurukshetra, Haryana 136 119, India

1-(Benzothiazol-2-yl)-4-phenylindeno[1,2-*c*]pyrazoles (**1**) and 1-(4-arylthiazol-2-yl)-4-phenylindeno[1,2-*c*]pyrazoles (**2**) have been synthesised by the reaction between 1-oxo-3-phenylindan-2-carboxaldehyde (**4**) and 2-hydrazinobenzothiazoles or 2-hydrazinothiazoles.

Keywords: fused pyrazoles, fused indenes; β-ketoaldehydes, 2-hydrazinobenzothiazoles, 2-hydrazinothiazoles

The synthesis of antipyrine, a pyrazole derivative, as a potent analgesic-antipyretic by Knorr[1] in 1883 initiated a widespread effort by chemists all over the world to search for more pyrazole derivatives possessing various physiological properties. These efforts led to the synthesis of a wide variety of pyrazole derivatives displaying diverse biological activities. The discovery of Fried *et al*.[2] that the anti-inflammatory activity of cortisone and other steroids increases dramatically on incorporation of a pyrazole nucleus drew the attention of scientists toward the synthesis of fused pyrazoles. A large number of fused pyrazoles such as steroidal pyrazoles, pyrimidinopyrazoles, pyrazoloquinolines, pyrazolobenzotriazine 5-oxides and indenopyrazoles have been reported to possess various biological properties such as anticancer,[3,4] herbicidal,[5] antiarrhythmic and antiinflammatory[6] effects. Appreciation of these findings, coupled with the observation that several benzothiazole and thiazole derivatives with a pyrazolyl moiety attached to position 2 of the benzothiazole and thiazole nucleus possessed significant biological properties, we report herein the synthesis of 1-(benzothiazol-2-yl)-4-phenylindeno[1,2-*c*]pyrazoles (**1**) and 1-(4-arylthiazol-2-yl)-4-phenylindeno[1,2-*c*]pyrazoles (**2**).



Scheme 1

Results and discussion

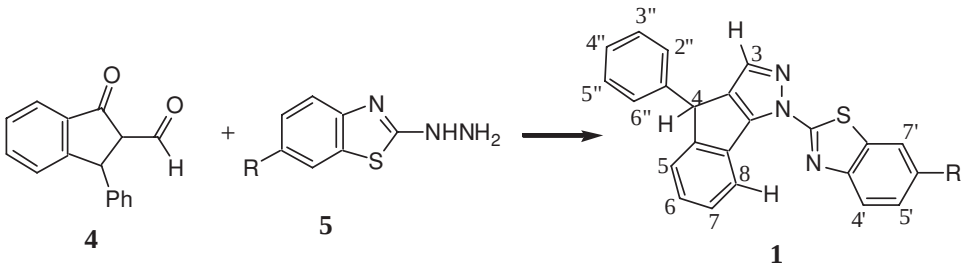
One of the most widely used methods for the synthesis of pyrazoles involves condensation of appropriate hydrazines and 1,3-diketones. The mechanism of this apparently simple reaction still evokes a lot of interest in the scientific community as complications are encountered in the delineation of reaction pathways when a substituted hydrazine and an unsymmetrical 1,3-diketone react, potentially leading to two isomeric pyrazoles substituted either at N1 or N2.

The present study concerns the preparation of thiazolyl and benzothiazolyl pyrazoles fused to the five-membered ring of the indene system. 1-Oxo-3-phenylindan-2-carboxaldehyde (**4**)[7] needed for the purpose has been synthesised by the reaction of 3-phenylindan-1-one (**3**) with ethyl formate in the presence of sodium ethoxide. The 3-phenylindan-1-one (**3**) was obtained, albeit in poor yield (22%), by the Friedel–Crafts reaction of cinnamic acid in dry benzene (Scheme 1).[8,9]

Various 2-hydrazinobenzothiazoles[10] (**5**) and 2-hydrazinothiazoles[11,12] needed for the present study were prepared according to the literature procedures. 1-(Benzothiazol-2-yl)-4-phenylindeno[1,2-*c*]pyrazoles (**1**) were prepared by the reaction between 1-oxo-3-phenylindan-2-carbaldehyde (**4**) and 2-hydrazinobenzothiazoles as shown in Scheme 2.

In principle, the condensation of either of the two nitrogen atoms of the hydrazine can occur either on the formyl group or on the C1 carbonyl group of 1-oxo-3-phenylindan-2-carboxaldehyde (**4**). Braun and Mosher[13] have reported that the condensation of 2-acetylindan-1,3-dione (**6**) and 2-propionylindan-1,3-dione (**7**) with hydrazine hydrate occurs on the side chain carbonyl group, furnishing hydrazones **8** and **9** respectively. Similar results were observed by Mosher and Bechara[14] on condensation of phenylhydrazine with 2-isvalerylindan-1,3-dione (**10**), yielding the hydrazone **11**. However, an apparently similar reaction between 2-(diphenylacetyl)indan-1,3-dione (**12**) and phenylhydrazine yielded a monohydrazone (**13**) in which the hydrazine moiety got attached to one of the indan-1,3-dione ring carbonyl groups.[14] This change in behaviour on altering the bulk of the side chain was attributed to steric interactions. It was proposed that in the diphenylacetyl compound **12** the two phenyl groups shield the side chain carbonyl group, thereby directing the nucleophilic attack by phenylhydrazine to the less hindered 1- or 3- carbonyl group instead of the side chain carbonyl group. In our case, as there are no such steric interactions present in the side chain, it is reasonable to assume that the initial condensation of 2-hydrazinobenzothiazole (**5**) with 1-oxo-3-phenylindan-2-carboxaldehyde (**4**) would occur on the side chain aldehyde rather than the ring carbonyl group. Furthermore, the secondary nitrogen atom is less nucleophilic than primary nitrogen atom, the most probable route for this reaction seems to be that leading to the formation of 1-(benzothiazol-2-yl)-4-phenylindeno[1,2-*c*]pyrazole (**1a**) as outlined in Scheme 2.

* Correspondent. E-mail: karansinghji@rediffmail.com
Present address: Medicinal Chemistry (NCER), Lupin Limited (Research Park), S. No. 46/47A, Village Nande, Taluka-Mulshi, Pune-42, Maharastra (India).



1,5 a; R=H
b; R=CH_3
c; R=OCH_3
d; R=Cl

Scheme 2

Furthermore, Belevich *et al.*[15] have reported the formation of a single product, the 1-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-one (**14a**) on reacting 2-formylindan-1,3-dione (**14**) with phenylhydrazine. Here the initial condensation apparently occurred on the formyl rather than a ring carbonyl group, otherwise, 2-substituted indeno[1,2-*c*]pyrazol-4(1*H*)-one (**14b**) would have resulted. However, a similar reaction between 2-formylindan-1-one (**15**) and 4-fluorophenylhydrazine is reported to occur by initial attack both on the ring and the aldehyde carbonyl groups, resulting in a mixture of both 1-substituted indeno[1,2-*c*]pyrazole (**15a**) and 2-substituted indeno[1,2-*c*]pyrazole (**15b**).[6] This observation of Hamilton[6] raised serious doubts in our minds about the possibility of formation of both the isomeric indenopyrazoles (**1**, **1'**) as our substrate (1-oxo-3-phenylindan-2-carbaldehyde **4**) is similar to that of Hamilton (**15**) rather than that of Belevich *et al.*[24]

In the event, condensation of equimolar amounts of 1-oxo-3-phenylindan-2-carboxaldehyde (**4**) with 2-hydrazinobenzothiazole (**5a**) in absolute ethanol-acetic acid (1 : 1) yielded only a single product as confirmed by thin layer chromatography (TLC) and the ^{1}H NMR spectra. The structure of this product was assigned as 1-(benzothiazol-2-yl)-4-phenylindeno[1,2-*c*]pyrazole (**1a**), based on a rigorous analysis of its 300MHz ^{1}H NMR spectrum. The most distinguishing feature of ^{1}H NMR spectrum of **1a** was a sharp one-proton singlet at δ 7.65 which can be ascribed only to C_3–H of the indenopyrazole ring system. Had it been the isomeric 2-subsituted-4-phenylindeno[1,2-*c*]pyrazole (**1'a**), the signal for C_3–H should have appeared further downfield at around δ 8.15. This argument finds rationale from earlier observations of Elguero *et al.*[16] who demonstrated that the presence of a heterocyclyl moiety at N2 of the pyrazole ring is responsible for deshielding of the C3–H signal. Moreover, C3–H and C4–H of the indenopyrazole ring system are expected to appear as doublets due to allylic coupling in the case of 2-substituted isomer **1'a** rather than two singlets as observed. These observations all support the structure **1a** for the isolated product.

Another characteristic feature of the ^{1}H NMR spectrum was a one-proton double doublet centered at δ 8.93 (J = 8.0, 2.0 Hz). Such high deshielding must be owing to electronic and/or steric factors. Inspection of a model of **1a** revealed that C8–H and the lone pair of electrons on the sulfur or the nitrogen atom of the benzothiazole moiety are in sufficiently close proximity to effect such a deshielding. There should have been no such deshielding of C8–H had the product been **1'a**, in which the nitrogen or sulfur of the benzothiazole moiety is remote from C8–H. This is consistent with an observation of Hamilton *et al.*[6] that even the presence of a much smaller phenyl group at N1 pushed C8–H in indenopyrazole to a lower field, while no such effect was observed when the phenyl group was located at N2.

The above observations provide convincing evidence that the product isolated in our case is the 1-substituted (**1a**) and not the 2-substituted isomer (**1'a**).

An attempt was also made to isolate the intermediate hydroxypyrazoline by performing the reaction between 1-oxo-3-phenylindan-2-carboxaldehyde (**4**) and 2-hydrazinobenzothiazole (**5a**) in absolute ethanol. A yellow solid mass was obtained after 30 min. reflux. Unfortunately, only a weak 300 MHz ^{1}H NMR spectrum, too complicated to be interpreted, of this material could be recorded because of its poor solubility in most of the commonly used NMR solvents. However, to our surprise this yellow solid mass provided compound **1a** (identical with a sample obtained by the direct route by ^{1}H NMR and mixed melting point) on refluxing in ethanol – acetic acid (1 : 1) for 15 h.

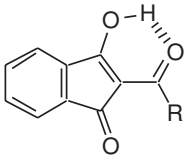
Other compounds in this series (**1b–1d**, **2a–2c**) were prepared following the procedure similar to that adopted for **1a** by the reaction between 1-oxo-3-phenylindan-2-carboxaldehyde (**4**) and the appropriate hydrazines. Their elemental analyses and spectral data were consistent with the assigned structures of all the new compounds.

Experimental

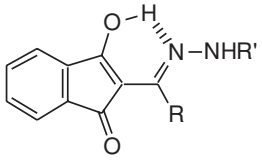
^{1}H NMR spectra were recorded on a Bruker 300 MHz instrument as $CDCl_3$ or DMSO-d_6 solutions using TMS as internal standard. Chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. IR spectra were recorded using KBr disks with a Buck Scientific IR M-500 IR spectrometer. High-resolution mass spectra were measured on a Kratos MS-50 mass spectrometer.

3-Phenylindan-1-one (**3**): $AlCl_3$ (250 g) was added in small portions to a vigorously stirred suspension of cinnamic acid (85g, 0.57 mol) in dry benzene (375 ml) and the solution was heated under reflux for 14 h. When evolution of HCl ceased the mixture was poured into ice-cold dil. HCl and shaken with ether and the organic layer washed with aqueous K_2CO_3, dried, and distilled, leaving 3-phenyl indan-1-one which upon crystallisation from light petroleum melted at 77 °C (lit.[8,9] m.p. 77–78 °C).

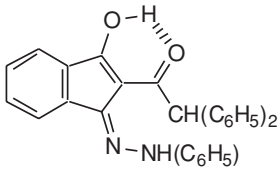
1-Oxo-3-phenylindan-2-carboxaldehyde (**4**): Ethyl formate (12 g) was added to an ice-cold suspension of sodium ethoxide (from 2.5 g of sodium) in benzene (250 ml) with shaking. A solution of 3-phenylindan-1-one (22.2 g) was added dropwise over 30 minutes with continuous shaking when a scarlet-coloured solid began to form. After keeping for 4 h at 0–5 °C the reaction mixture was decomposed with water (200 ml). The benzene layer was separated and the aqueous layer was washed with more benzene (100 ml). The aqueous layer was acidified with dil. HCl and the oil which separated was taken up in ether. The ethereal layer was washed with water and dried ($MgSO_4$). Evaporation of the solvent provided of 1-oxo-3-phenylindan-2-carboxaldehyde (19.8 g, 78%) which upon crystallisation from benzene melted at 128 °C (Lit.[7] m.p. 129–130 °C).



6; R=CH_3
7; R=C_2H_5
10; R=$CH_2CH(CH_3)_2$
12; R=$CH(C_6H_5)_2$



8; R=CH_3, R'=H
9; R=C_2H_5, R'=H
11; R=$CH_2CH(CH_3)_2$, R'=C_6H_5



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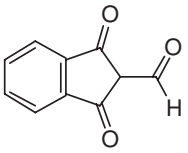

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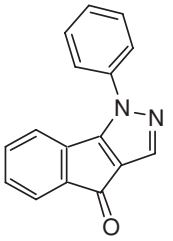
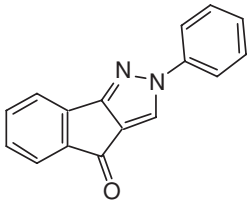
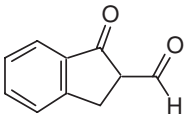


14a



14b



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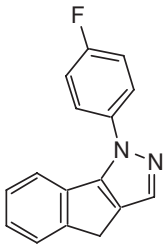
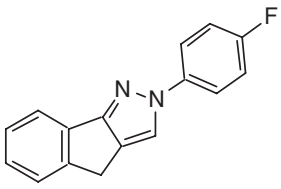
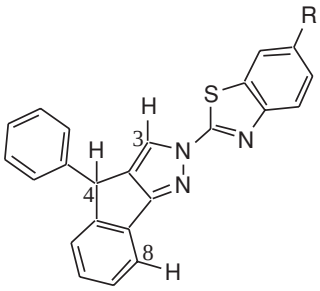


15a



15b



1'

2-Hydrazinobenzothiazole (**5a**): To hydrazine hydrate (0.2 mol) was added HCl (10 ml) dropwise with stirring at 5–10 °C. Ethylene glycol (40 ml) was then added followed by 2-aminobenzothiazole (0.05 mol) in portions to the above reaction mixture and the resulting mixture was refluxed for 2 h. A fine crystalline solid which separated out on cooling was filtered, washed with water and crystallised from ethanol, m.p. 194 °C (Lit.[10] m.p. 195 °C), yield 65%.

6-Methyl-2-hydrazinobenzothiazole (**5b**): m.p. 213 °C (Lit.[10] m.p. 214 °C), yield 75%.

6-Methoxy-2-hydrazinobenzothiazole (**5c**): m.p. 167 ºC (Lit.[10] m.p. 168–169 °C), yield 74%.

6-Chloro-2-hydrazinobenzothiazole (**5d**): m.p. 215 °C (Lit.[10] m.p. 215–216 °C), yield 78%.

2-Hydrazinothiazole

2-Aminothiazole (10g, 0.1 mol) was dissolved in concentrated HCl (80 ml) and diazotised by slow addition of saturated aqueous sodium nitrite (7g, 0.1 mol) with vigorous stirring while maintaining the internal temperature between –10 to 5 °C. The diazonium solution thus obtained was reduced with a solution of stannous chloride dihydrate (45 g, 0.2 mol) in concentrated HCl (20 ml). During the reduction the temperature was kept around –10 °C. The yellowish viscous material which separated was decanted off, sucked dry and washed throughly with dry ether.

The above salt was then covered with benzene (1 l) and ammonia gas passed through the solution for 10 min to expel oxygen. Water (10 ml) was then added and the benzene solution was saturated with ammonia gas for 3 h with occasional shaking. The resulting solution was filtered from undissolved material and dried over anhydrous $MgSO_4$. Excess of benzene was removed under reduced pressure until the separation of a solid began. Precipitation was completed by the addition of petroleum ether to give 2-hydrazinothiazole, yield 4 g (35%), m.p. 96–98 °C (lit.[11] m.p. 97–98 °C).

4-Aryl-2-hydrazinothiazoles: A mixture of 4-substituted-2-chlorothiazole (0.06 mol), pyridine (6 ml) and hydrazine hydrate (15 ml) in ethanol (60 ml) was heated under reflux for 3h. The solvent was removed under reduced pressure. The residual mass was poured on crushed ice and the solid thus obtained was crystallised from ethanol.

4-Phenyl-2-hydrazinothiazole: m.p. 168 °C (lit.[12] m.p. 169 °C), yield 60%.

4-(4-Nitrophenyl)-2-hydrazinothiazole: mp 176 °C (lit.[12] m.p. 176 °C), yield 65%.

General procedure for synthesis of indeno[1,2-c]pyrazoles (**1**, **2**): A mixture of *N*-substituted hydrazine (0.005 mol) and 1-oxo-3-phenylindan-2-carboxaldehyde (0.005 mol) in absolute ethanol-acetic acid (1 : 1) was refluxed for 10 h. The separated solid was filtered, washed with cold ethanol and crystallised from $CHCl_3$–EtOH.

1-(Benzothiazol-2-yl)-4-phenylindeno[1,2-c]pyrazole (**1a**): m.p. 196–198 °C; yield 44%; IR (KBr): no absorption in the region 1620–1800 cm^{-1} (C=O str. absent); ^1H NMR ($CDCl_3$, 300 MHz): d 4.96 (s, 1H, C4–H), 7.18–7.56 (m, 10H, C5–H, C6–H, C7–H, C5'–H, C6'–H, C2''–H, C3''–H, C4''–H, C5''–H and C6''–H), 7.65 (s, 1H, C3–H), 7.89 (d, 1H, *J* = 7.8 Hz, C7'–H), 8.08 (d, 1H, *J* = 7.8 Hz, C4'–H), 8.93 (dd, 1H, *J* = 8.0, 2.0 Hz, C8–H); MS: M^+ *m/z* 365.0985; Calcd. 365.0986. Anal. Found: C, 75.19; H, 4.24; N, 10.98. Calcd. for $C_{23}H_{15}N_3S$: C, 75.59; H, 4.14; N, 11.48 %.

1-(6-Methylbenzothiazol-2-yl)-4-phenylindeno[1,2-c]pyrazole (**1b**): m.p. 202–203 °C; yield 48%; IR (KBr): no absorption in the region 1620-1800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): d 2.52 (s, 3H, C6'–CH_3), 4.95 (s, 1H, C4–H), 7.19 (dd, 1H, *J* = 8.4, 2.0 Hz, C5'–H), 7.27–7.55 (m, 8H, C5–H, C6–H, C7–H, C2''–H, C3''–H, C4''–H C5''–H and C6''–H), 7.63 (s, 1H, C3–H), 7.68 (s, 1H, C7'–H), 7.96 (d, 1H, *J* = 8.4 Hz, C4'–H), 8.91 (dd, 1H, *J* = 8.1, 1.9 Hz, C8–H); Anal. Found: C, 75.69; H, 4.34; N, 10.69. Calcd. for $C_{24}H_{17}N_3S$: C, 75.96; H, 4.52; N, 11.08 %.

1-(6-Methoxybenzothiazol-2-yl)-4-phenylindeno[1,2-c]pyrazole (**1c**): m.p. 244–246 °C; yield 40%; IR (KBr): no absorption in the region 1620–1800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): d 3.92 (s, 3H, C6'–OCH_3), 4.95 (s, 1H, C4–H), 7.12 (dd, 1H, *J* = 8.7, 2.5 Hz, C5'–H), 7.18–7.32 (m, 6H, C5–H, C6–H, C7–H, C3''–H, C4''–H and C5''–H), 7.36 (d, 1H, *J* = 2.5 Hz, C7'–H), 7.44–7.50 (m, 2H, C2''–H, C6''–H), 7.63 (s, 1H, C3–H), 7.95 (d, 1H, *J* = 8.7 Hz, C4'–H), 8.89 (dd, 1H, *J* = 8.0, 2.2 Hz, C8–H); MS: M^+ 395.1091; Calcd. 365.1092. Anal. Found: C, 72.59; H, 4.08; N, 10.57. Calcd. for $C_{24}H_{17}N_3OS$: C, 72.89; H, 4.33; N, 10.63 %.

1-(6-Chlorobenzothiazol-2-yl)-4-phenylindeno[1,2-c]pyrazole (**1d**): m.p. 223–224 °C; yield 45%; IR (KBr): no absorption in the region 1620–1800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): d 4.96 (s, 1H, C4–H), 7.19 (dd, 1H, *J* = 7.8, 2.0 Hz, C5'–H), 7.28–7.50 (m, 6H, C5–H, C6–H, C7–H, C2''–H, C3''–H, C4''–H, C5''–H, C6''–H), 7.65 (s, 1H, C3–H), 7.86 (d, 1H, *J* = 2.0 Hz, C7'–H), 7.98 (d, 1H, *J* = 7.8 Hz, C4'–H), 8.87 (dd, 1H, *J* = 8.7, 2.1 Hz, C8–H); MS: M^+ *m/z* 399/401. Anal. Found: C, 69.18; H, 3.21; N, 10.01. Calcd. for $C_{23}H_{14}ClN_3S$ (399.90): C, 69.08; H, 3.53; N, 10.50 %.

1-(Thiazol-2-yl)-4-phenylindeno[1,2-c]pyrazole (**2a**): m.p. 121–122 °C; yield 49%; IR (KBr) cm^{-1}: IR (KBr): no absorption in the region 1620–1800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): d 4.86 (s, 1H, C4–H), 7.09–7.10 (d, 1H, *J* = 3.5 Hz, C5'–H), 7.12–7.38 (m, 9H, C3, 5, 6, 7, 2", 3", 4", 5" 6"–H), 7.66–7.67 (d, 1H, *J* = 3.5 Hz, C4'–H), 8.71–8.73 (dd, 1H, *J* = 7.6, 1.7 Hz, C8–H); Anal. Found: C, 72.59; H, 4.04; N, 12.98. Calcd. for $C_{19}H_{13}N_3S$: C, 72.36; H, 4.15; N, 13.33 %.

1-*(4-Phenylthiazol-2-yl)-4-phenylindeno[1,2-c]pyrazole* (**2b**): m.p. 188–190 °C; yield 48%; IR (KBr): no absorption in the region 1620–1800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): d 4.91 (s, 1H, C4–H), 7.15–7.51 (m, 12H, C3, 5, 6, 7, 2", 3", 4", 5", 6", 3"', 4"', 5"'–H), 7.56 (s, 1H, C5'–H), 7.96–7.99 (d, 2H, *J* = 7.5 Hz, C2"', 6"'–H), 8.82–8.85 (dd, 1H, *J* = 7.7, 1.6 Hz, C8–H); Anal. Found: C, 76.59; H, 4.14; N, 10.40. Calcd. for $C_{25}H_{17}N_3S$: C, 76.70; H, 4.38; N, 10.74 %.

1-[4-(4-Nitrophenyl)thiazol-2-yl]-4-phenylindeno[1,2-c]pyrazole (**2c**): m.p. 240–242 °C; yield 40%; IR (KBr): no absorption in the region 1620–1800 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz): d 4.90 (s, 1H, C4–H), 7.10–7.44 (m, 8H, C5, 6, 7, 2', 3", 4", 5", 6"–H), 7.47 (s, 1H, C3–H), 7.56 (s, 1H, C5'–H), 8.12–8.15 (d, 2H, *J* = 8.7 Hz, C2"', 6"'–H), 8.36–8.39 (d, 2H, *J* = 8.7 Hz, C3"' 5"'–H), 8.68–8.71 (dd, 1H, *J* = 6, 1.5 Hz, C8–H). Anal. Found: C, 68.59; H, 3.51; N, 12.94; Calcd. for $C_{25}H_{16}N_4O_2S$: C, 68.79; H, 3.69; N, 12.84 %.

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