

A preparation, Characterization of some new 5 - X¹ - 3 (4 - X² - Phenacylidene) oxindole

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Abstract

A new compounds of 5 - X¹ - 3 (4 - X² - Phenacylidene) oxindole were prepared by condensation of p-substituted acetophenone with 5-substituted isatin by Knoevenage reaction by two steps, the first step is include the preparation of 5-X¹- 3 (4 - X² - 3 - hydroxyl phenacyl) oxindoles and the second, prepared the products, 5- X¹ - 3 (4 - X² - phenacylidine) oxindole, X¹ - X² represented (CH₃ - H) (1), (CH₃ - CH₃) (2), (CH₃ - OCH₃) (3), (CH₃ - Cl) (4), (CH₃ - Br) (5), (Cl - Cl) (6) and (Br - Br) (7).

These compounds were characterized by physical and spectroscopic methods such ¹³CNMR and IR in solid state. The wave number of stretching vibration for carbonyl group was determined in CHCl₃ solvent.

acetophenone in the presence of diethyl amine as a basic catalyst. Correlation analysis and physical properties for these compounds are studied.

The aim of the present work is to extend the synthesise of new 5- X¹-3 (4- X² - phenacylidene) oxindole. The spectroscopic data of the new compounds are reported.

Experimental work.

A-The preparation

1) 5 - X¹ - 3 (4- X² - 3 - hydroxyl phenacyl) oxindole (1) and derivatives.

Five grams of 5 - methyl isatin and an equimolecular amount of p-x-acetophenone (X = H, Me, OMe, Cl and Br) were dissolved in 100 ml of absolute alcohol and in the presence of diethyl amine (10 drops) (1ml) was added slowly. The mixture was allowed to stand overnight at room temperature. The orange needles were formed then separated by filtration and recrystallized from ethyl alcohol.

This procedure was also followed in the reaction of 5 - chloro and 5 - bromo isatin with para-(chloro and bromo) acetophenone (Table-1).

2) 5-X¹-3 (4-X²- Phenacylidene) oxindole.

A mixture containing 8 gm of 5-X¹-3 (4-X²- hydroxyl phenacyl) oxindole (compound no. 1), 25 ml of alcohol and 50 ml of conc. HCL were allowed to stand overnight. The fine red needles of product was formed. The product was recrystallized from ethyl alcohol. This procedure was also used in the case of certain derivatives of compounds no. 1 (Table 2).

B) Physical measurements :

The analytical measurements for C, N and H elements were carried out by AE- 1108 carlo Erba CHN analyser. IR spectra were recorded by using KBr discs in the range 4000-200 cm⁻¹ on a pye-Unicam SP 3-300. Infrared Spectrophotometer in Slovak Technical University. While infrared in solution were measured at room temperature in the region of 1800-1600 cm⁻¹ using a Zeiss Specrod M 80 spectrometer. The measurements were carried out in CHCl₃ employing NaCl of 1.0 and 5.0

mm thickness. CHCl_3 was of spectral purity (Uvasol, Merck). The concentration of the solution were chosen to reach a maximum of absorption of 75–80%. Positions were determined with accuracy of $\pm 0.2 \text{ cm}^{-1}$. ^{13}C -NMR measurements were run for 0.1 M DMSO- d_6 solution at 30°C with a Bruker Avance DRX 500 FT NMR Spectrometer in Slovak Technical University.

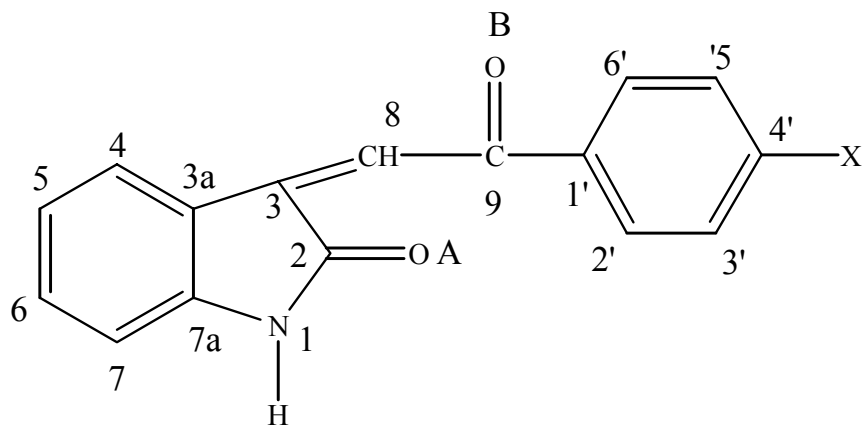


Table 1. Physical properties and data for 5-X¹-3 (4⁻X²-3- hydroxyl phenacyl) oxindoles (1) and its derivatives .

Com. No.	X ¹	X ²	Formula	Yield	M.P. °C	Analysis found (cacul.)%		
						C	N	H
1	CH ₃	H	C ₁₇ H ₁₅ O ₃ N	70	80-82	72.51 (72.53)	4.714(4.98)	5.2 (5.37)
2	CH ₃	CH ₃	C ₁₀ H ₁₇ O ₃ N	75	90-91	73.60 (73.20)	4.69 (4.74)	5.81 (5.80)
3	CH ₃	OCH ₃	C ₁₈ H ₁₇ O ₄ N	60	90-93	69.51 (69.44)	5.02 (4.49)	5.44 (5.50)
4	CH ₃	CL	C ₁₇ H ₁₄ O ₃ NCl	75	88-90	64.70 (64.66)	4.50 (4.43)	4.41 (4.46)
5	CH ₃	Br	C ₁₇ H ₁₄ O ₃ NBr	70	79-80	56.11 (56.68)	3.79 (3.88)	3.98 (3.91)
6	CL	CL	C ₁₆ H ₁₁ O ₃ NCl ₂	65	90-92	57.61 (57.16)	4.17 (4.16)	3.31 (3.29)
7	Br	Br	C ₁₆ H ₁₁ O ₃ NBr ₂	60	91-93	45.17 (45.20)	3.11 (3.29)	2.68 (2.60)

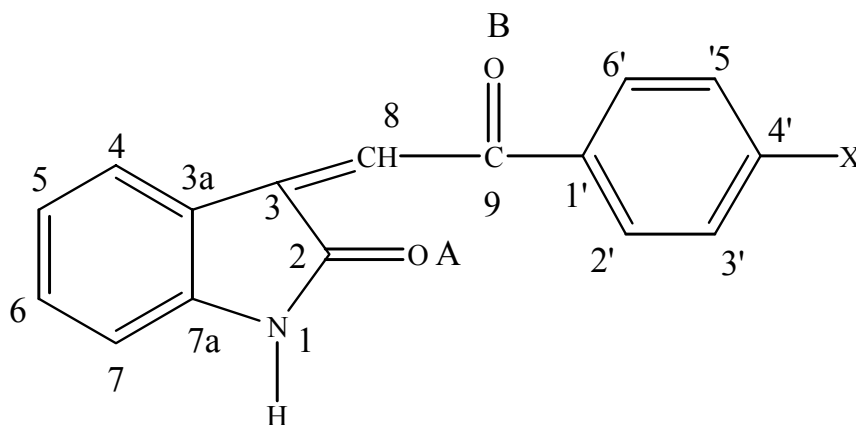


Table 2. Physical properties, yields and analytical data for 5-X¹-3 (4-X² - Phenacyclidine) oxindole.

Com.N o.	Formula	m.p. °C	yield	Anal. Found (cacl.) %		
				C	H	N
1 ^o	C ₁₇ H ₁₃ O ₂ N	189	70	77.12 (77.60)	4.50 (4.97)	5.17 (5.32)
2 ^o	C ₁₈ H ₁₅ O ₂ N	201	70	77.80 (77.95)	5.11 (5.45)	4.99 (5.05)
3 ^o	C ₁₈ H ₁₅ NO ₃	169	75	73.33 (73.70)	5.30 (5.15)	4.50 (4.77)
4 ^o	C ₁₇ H ₁₂ O ₂ NCl	170	70	68.23 (68.57)	4.33 (4.06)	4.10 (4.70)
5 ^o	C ₁₇ H ₁₃ O ₂ NBr	200	60	59.12 (59.67)	3.65 (3.53)	4.20 (4.09)
6 ^o	C ₁₆ H ₉ O ₂ NCl ₂	192	65	60.22 (60.40)	2.77 (2.85)	4.13 (4.40)
7 ^o	C ₁₆ H ₉ NBr ₂	177	60	47.61 (47.21)	2.12 (2.22)	3.40 (3.45)

¹³C NMR Spectroscopy :

The assignment of ¹³C NMR spectra of the prepared compounds are identified comparing them with oxindoles (Gassman et al. 1977), indoles (Cohien et al. 1960; Stother, 1972; Balsells and Frasca, 1989), isatin (Gassman et al. 1977; Radhy et al. 2001), 2 (4- substituted phenyl isatogenes (Stoddart and Hopper, 1989) and substituted ---2- thiophene carboxanilides (Maria et al. 1989). Table 3. gives C¹³ chemical shift of these compounds.

IR Spectra in Solution :

The characteristic infrared spectra data of the prepared compounds measured in diluted solution of trichloromethane is listed in Table 4 .

Table 3. C-Chemical Shifts for 5-X¹-3 (4 - X²- Phenacylidene) oxindole

Com p. no.	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C _{7a}	C _{3a}	C ₈	C ₉	C ₁	C _{2,6}	C _{5,3}	C ₄	CH ₃	OCH ₃
1	192.0	133.0	124.9	132.0	121.8	111.0	145.1	121.0	125.0	168.0	137.1	129.1	128.1	133.9	21.1	
2	190.5	130.4	126.1	132.0	127.1	110.1	144.5	133.0	125.1	168.0	133.2	129.7	128.6	142.7	21.3	
3	189.0	130.4	126.1	129.0	127.1	109.1	140.5	133.0	129.0	168.9	129.0	130.1	129.8	142.5	21.7	45
4	190.0	138.3	124.4	120.1	121.0	109.0	144.5	120.0	129.1	168.0	134.8	131.6	129.1	140.4	22.1	
5	191.5	137.4	125.2	128.8	121.0	109.2	142.0	120.0	127.0	166.8	133.9	132.9	127.1	150.1	21.2	
6	189.0	138.5	126.7	135.0	121.8	111.0	144.0	121.0	126.7	167.8	136.2	129.9	128.8	138.5		
7	190.0	134.9	127.7	133.8	125.2	110.9	142.5	124.0	127.7	168.0	130.0	134.2	131.8	145.3		

Table 4. Infrared Spectra Data (cm⁻¹) for 5-X¹-3 (4⁻-X² – Phenacylidene) oxindol .

Comp. No.	$\nu(\text{C}=\text{O})^{\text{A}}$	$\nu(\text{C}=\text{O})^{\text{B}}$	$\nu \text{C}=\text{C}$
1 ⁻	1722.0	1664.5	1620.2
2 ⁻	1721.6	1666.4	1619.2
3 ⁻	1730.3	1657.6	1627.2
4 ⁻	1730.4	1658.0	1618.0
5 ⁻	1728.2	1660.8	1627.2
6 ⁻	1729.0	1664.4	1619.2
7 ⁻	1728.0	1660.4	1620.0

The compounds clearly exhibit in the region of 1730-1620 cm⁻¹, three variable absorption bands of strong to medium intensity. The first which the highest wave number band in 1720-1730 cm⁻¹ region can be assigned to stretching vibration of the oxindole ring C = O group A ($\nu \text{C} = \text{O}$)^A. this well agrees with other oxindole derivatives (Kellie etal.1956;Stother,1972;Kostarial and Perjessy,1976). The second which is the variable medium intensity wave number band in the spectra of compounds (1 to 7) in 1670-1660 cm⁻¹ region belongs to the stretching vibration of strongly conjugated C = O group B in the substituted –2-Phenacylidene moiety, i. e. $\nu (\text{C} = \text{O})^{\text{B}}$. the third which is the medium intensity and lowest wave number band 1620-1630 cm⁻¹ should be assigned to stretching vibration of C = C bond in the phenacylidene, i. e. $\nu \text{C} = \text{C}$. This can be seen in Table 4

IR Spectra in Solid State :

The infrared spectra (KBr disc) of all compounds show absorption bands near 3400-3200 cm⁻¹ belonging to $\nu \text{N-H}$ stretching as illustrated in Table 5. Two strong absorption owing to carbonyl stretching vibration, the first occurs at 1740-1720 cm⁻¹ due to C = O^A ($\nu \text{C} = \text{O}$)^A and the second occurs at 1680-1660 cm⁻¹ due to ($\nu \text{C} = \text{O}$)^B .

C = C stretching vibration appears at 1640-1620 cm^{-1} while C = C aromatic stretching vibration occurs at 1620-1580 cm^{-1} .

In addition to these absorption peaks, there are a number of characterized absorption of substituted benzene ring, such as C-Br and C-Cl stretching at 750 and 820 cm^{-1} respectively. OCH_3 group is characterized by C-O-C asy. and sym. stretching at 1200 and 1100 cm^{-1} respectively as strong peak.

Asy. and sym. C-H stretching of methyl group appears at 2920 and 2890 cm^{-1} respectively and C-H bending of CH_3 at 1610 cm^{-1} .

Table 5. Carbonyl, C = C and N-H Stretching vibration in cm^{-1} for the 5-X¹- 3 (4-X²- Phenacylidene) oxindole.

Com. No.	$\nu\text{C} = \text{O}^{\text{A}}$	$\nu\text{C} = \text{O}^{\text{B}}$	$\nu\text{C} = \text{C}$	$\nu\text{N} - \text{H}$
1	1740.4	1680.0	1640.0	3300.0
2	1740.4	1670.0	1620.0	3400.0
3	1730.0	1670.0	1640.0	3200.0
4	1730.0	1660.0	1630.0	3300.0
5	1735.0	1680.0	1635.0	3200.0
6	1735.0	1690.0	1630.0	3400.0
7	1720.0	1680.0	1630.0	3300.0

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