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A preparation, Characterization of some new $5 – X^1 – 3$ $(4^{-} - X^2 –$ Phenacylidene) oxindole

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Abstract

A new compounds of $5 – X^1 – 3$ $(4^{-} - X^2 –$ 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 $5–X^1– 3$ $(4^{-} - X^2 – 3 –$ hydroxyl phenacy1) oxindoles and the second, prepared the products, $5- X^1 – 3$ $(4^{-} - X^2 –$ phenacylidine) oxindole, $X^1 – X^2$ represented (CH_3 – H) (1), (CH_3 – CH_3) (2), (CH_3 – OCH_3) (3), (CH_3 – Cl) (4), (CH_3 – Br) (5), (Cl – Cl) (6) and (Br – Br) (7).

These compounds were characterized by physical and spectroscopic methods such ^{13}CNMR and IR in solid state. The wave number of stretching vibration for carbony1 group was determined in $CHC1_3$ solvent.

تحضير وتشخيص مركبات جديدة لـ 5 – X^1 – 3 (4^- – X^2 – فيناسادين) اوكساندول

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الملخص

تم تحضير مركبات جديدة لـ 5 – X^1 – 3 (4^- – X^2 – فيناسادين) اوكساندول بطريقة تكثيف بارا معوض – اسيتو فينون مع 5 – معوض استاين بتفاعل نيو فانجيل المعروف بخطوتين الأولى تكوين 5 – X^1 – 3 (3 – X^2 – هيدروكسي فينا سايل) اوكساندول ثم تكوين الناتج بالمرحلة الثانية بعد فقدان جزيئة ماء حيث X^2 – X^1 هي تمثل :

(CH_3 – H) (1), (CH_3- CH_3) (2), (CH_3 – OCH_3) (3), (CH_3 – CI) (4), (CH_3 – Br) (5), (CI – CI) (6) and (Br – Br) (7).

تم تشخيص هذه المركبات بالطرق الفيزيائية والطيفية كطيف الرنين النووي المغناطيسي للكاربون – 13 وطيف الأشعة تحت الحمراء في الحالة الصلبة وكذلك تعيين العدد الموجي لتردد مجموعتي الكربونيل في الحالة السائلة في مذيب $CHCI_3$.

Introduction

The condensation of β – carbonyl of isatin molecule with various compounds have been studied by many authors (Lindwall and Maclernan,1932;Braude and Lindwall,1933;Percy and Helen,1953;Hinman and Bauman,1964; Bergman, 1971; Gassman etal.1977;Ibrahim etal.1997). Some of isatin derivatives for example pyrazoline, methathizon and pyrimidinethion are used in different biological and industrial aspects (Osden,1970; Paat,1977; Sharmon etal.1999).

(Radhy etal.2006; Lindwall and Maclernan,1932) have been prepared 3 – (4^- - X – Phenacylidine) oxindole, (X = H, Me, OMe, Br, Cl, NO_2 and NH_2), which are produced from condensation 5 – X – isatin with 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 synthesize of new 5- X^1 –3 (4^- - X^2 – phenacylidene) oxindole. The spectroscopic data of the new compounds are reported.

Experimental work.

A-The preparation

1) 5 – X^1 – 3 (4^- -X^2 - 3 – hydroxyl phenacyl) oxindole (1) and derivatives.

Five grams of 5 – methyl isatin and an equimolecular amount of p-x-acetophenoe (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 slowlely. The mixture was allowed to stand overnight at room temperature. The orange needles were formed then separated by filteration and recystallized 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-l).

2) 5-X^1-3 (4-X^2- Phenacylidene) oxindole.

A mixture containing 8 gm of 5-X^1-3 (4^--X^2- 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 Techenical 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 $CHCl_3$ 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%. Position were determined with accuracy of ± 0.2 cm^{-1} ^{13}C-NMR measurement were run for 0.1 M DMSO- d_6 solution at 30^0 C with a Broker Avance DRX 500 FT NMR Spectrometer in Slovak Technical University.

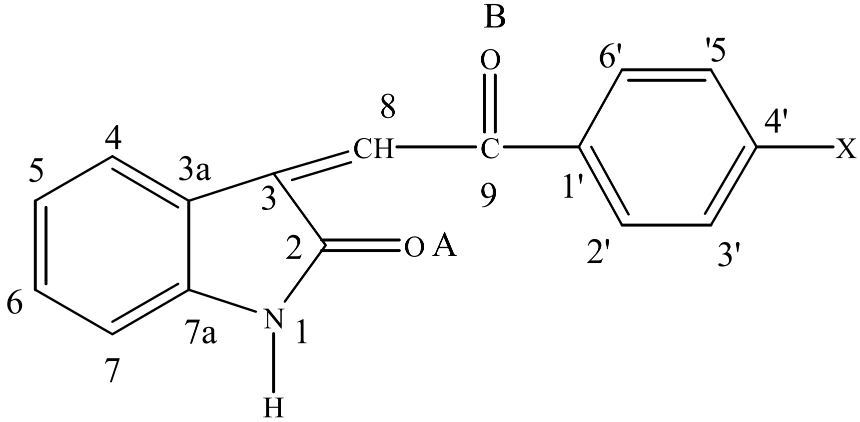


Table 1. Physical properties and data for 5-X^1-3 (4¯X^2-3- hydroxyl phenacyl) oxindoles (1) and its derivatives .

Com. No.	X^1	X^2	Formula	Yield	M.P. °C	Analysis found (cacul.)%		
						C	N	H
1	CH_3	**H**	$C_{17}H_{15}O_3N$	70	80-82	72.51 (72.53)	4.714(4.98)	5.2 (5.37)
2	CH_3	CH_3	$C_{10}H_{17}O_3N$	75	90-91	73.60 (73.20)	4.69 (4.74)	5.81 (5.80)
3	CH_3	OCH_3	$C_{18}H_{17}O_4N$	60	90-93	69.51 (69.44)	5.02 (4.49)	5.44 (5.50)
4	CH_3	CL	$C_{17}H_{14}O_3NCl$	75	88-90	64.70 (64.66)	4.50 (4.43)	4.41 (4.46)
5	CH_3	Br	$C_{17}H_{14}O_3NBr$	70	79-80	56.11 (56.68)	3.79 (3.88)	3.98 (3.91)
6	CL	CL	$C_{16}H_{11}O_3NCl_2$	65	90-92	57.61 (57.16)	4.17 (4.16)	3.31 (3.29)
7	Br	Br	$C_{16}H_{11}O_3NBr_2$	60	91-93	45.17 (45.20)	3.11 (3.29)	2.68 (2.60)

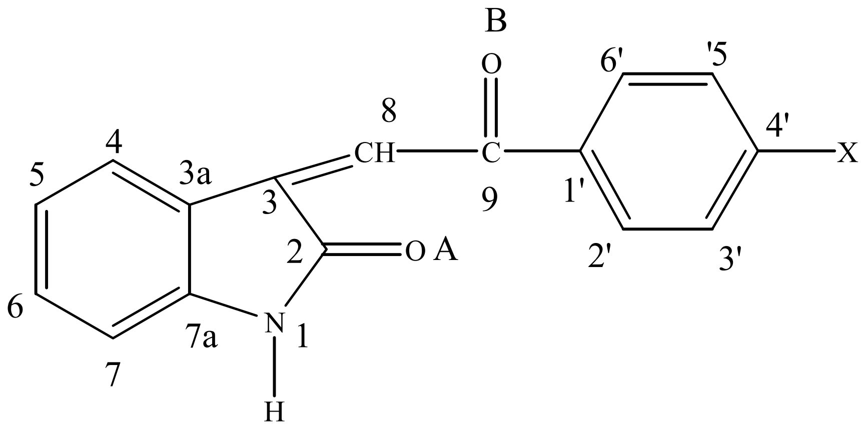
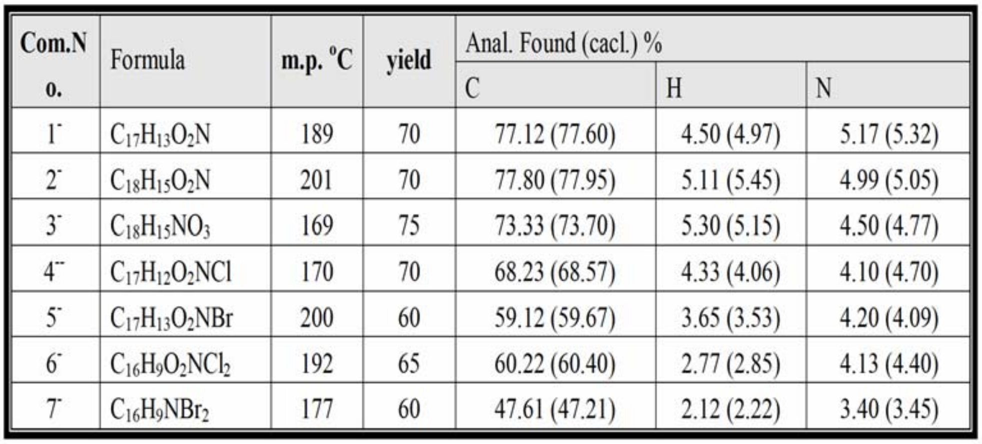


Table 2. Physical properties, yields and analytical data for 5-X^1-3 (4-X^2 - Phenacyclidine) oxindole.



Com.No.	Formula	m.p. °C	yield	Anal. Found (cacl.) %		
				C	H	N
1'	$C_{17}H_{13}O_2N$	189	70	77.12 (77.60)	4.50 (4.97)	5.17 (5.32)
2'	$C_{18}H_{15}O_2N$	201	70	77.80 (77.95)	5.11 (5.45)	4.99 (5.05)
3'	$C_{18}H_{15}NO_3$	169	75	73.33 (73.70)	5.30 (5.15)	4.50 (4.77)
4''	$C_{17}H_{12}O_2NCl$	170	70	68.23 (68.57)	4.33 (4.06)	4.10 (4.70)
5'	$C_{17}H_{13}O_2NBr$	200	60	59.12 (59.67)	3.65 (3.53)	4.20 (4.09)
6'	$C_{16}H_9O_2NCl_2$	192	65	60.22 (60.40)	2.77 (2.85)	4.13 (4.40)
7'	$C_{16}H_9NBr_2$	177	60	47.61 (47.21)	2.12 (2.22)	3.40 (3.45)

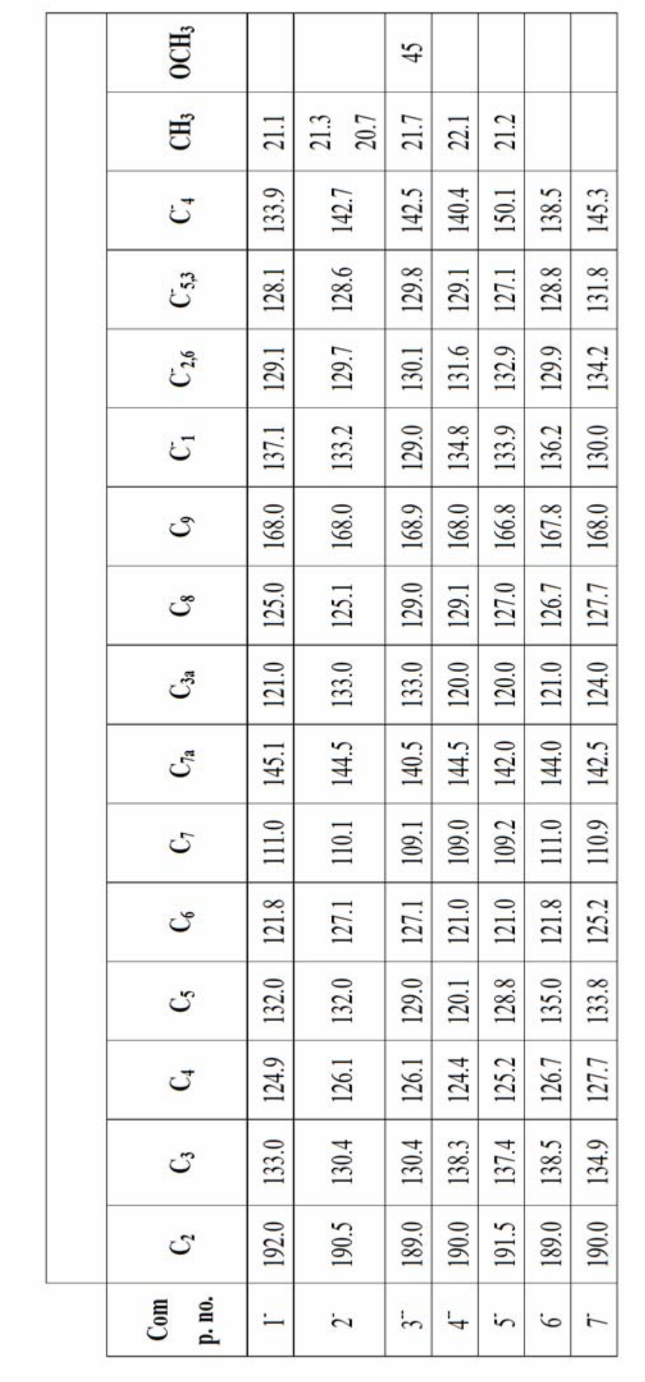
^{13}C NMR Spectroscopy :

The assignment of ^{13}C NMR spectra of the prepared compounds are identified camparing them them with oxindoles(Gassman etal.1977), indoles (Cohien etal.1960; Stother,1972;Balsells and Frasca,1989), isatin (Gassman etal.1977;Radhy etal.2001), 2 (4- substituted phenyl isatogenes (Stoddart and Hopper,1989) and substituted —-2- thiophene carboxanilides (Maria etal.1989). Table 3. gives C^{13} 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



Comp. 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 20.7	
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		

Table4. lnfrared Spectra Data (cm^{-1}) for 5-X^{1}-3 (4^{-} -X^{2} – Phenacylidene) oxindol .

Comp. No.	ν(c = o)^{A}	ν(c = o)^{B}	ν c = 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 (ν C = 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 ware 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. ν (C = O)$^{B.}$ the third which is the medium intensity and lowest ware number band 1620-1630 cm^{-1} should be assigned to stretching vibration of C = C bond in the phenacylidene, i. e νC = 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 νN-H stretching as illustrated in Table 5. Tow strong absorption owing to carbonyl stretching vibration, the first occurs at 1740-1720 cm^{-1} due to C = O^{A} (ν C = O)^{A} and the second occurs at 1680-1660 cm^{-1} due to (ν C = 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-X^1- 3 (4-X^2- Phenacylidene) oxindole.

Com. No.	$\nu C = O^4$	$\nu C = O^B$	$\nu C = C$	$\nu N - H$
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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