J. Coll. Sci., Univ. Riyadh, Vol. **11**, pp. 229 - 237 (1980)

Chelating Properties of 2-Acyl-1, 3-Indanediones, I. Synthesis and Physicochemical Parameters*

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In this study, 2-acyl-1,3-indanediones have been synthesized to investigate their chelating properties towards a number of transition metals and to assess their potentialities as analytical reagents for such metals. The synthesis of such compounds involves the condensation of dimethylphthalate with the appropriate ketone in the presence of methoxide ion. The physico-chemical properties of the title compounds have been studied. Those properties include: electronic absorption, vibrational absorption and proton magnetic resonance spectra. The pKa values of these compounds have been determined potentiometrically.

Acetylacetone (I) is a well-known chelating agent that gives stable chelates with most transition metals (Calvin and Wilson 1945). In this study, it was of interest to introduce its chelating groups into a cyclic form, 2-acyl-1-3-indanedione structure (II) was chosen. The incorporation of the chelating groups in a cyclic form would give metal chelates of higher stability and are more readily extractable in organic solvent. Furthermore, the high molecular weight of the metal chelates thus formed would increase the sensitivity of the analytical method to be developed.

In this communication, the synthesis and the physico-chemical properties of three analogues of structure (II), are reported.

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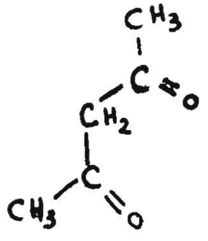
* Presented before the Joint Central — Great Lakes Regional Meeting of the American Chemical Society. May 24-26 (1978), Indianapolis, Indiana, U.S.A.
Organic Chemistry Section, Abstract // 19, p. 119.



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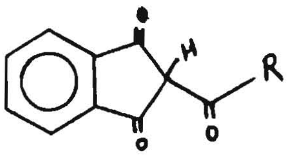


II

(1) *Synthesis*

The synthesis of the compounds were achieved according to the general method described by Kilgore *et al.* (1942). The melting points agree with those reported by Kilgore *et al.* (1942).

(2) *Spectrometric Studies*

Electronic absorption spectra in cyclohexane, ethanol and 0.1 *N* NaOH were obtained on Varian-Techtron UV-VIS recording spectrometer (model 635). The vibrational absorption spectra of the compounds (KBr pellets) were obtained on infrared spectrometer (Perkin Elmer model 567).

PMR spectra of the compounds in $CDCL_3$ and CCI using TMS as internal standard, were obtained on a Varian T60-A NMR spectrometer.

(3) *Determination of* pk_a

The pK_a values were determined in ethanol 95 % medium according to the method of Albert and Serjeant (1971) using EIL pH-meter model 7050 equipped with combination electrode.

Results and Discussion

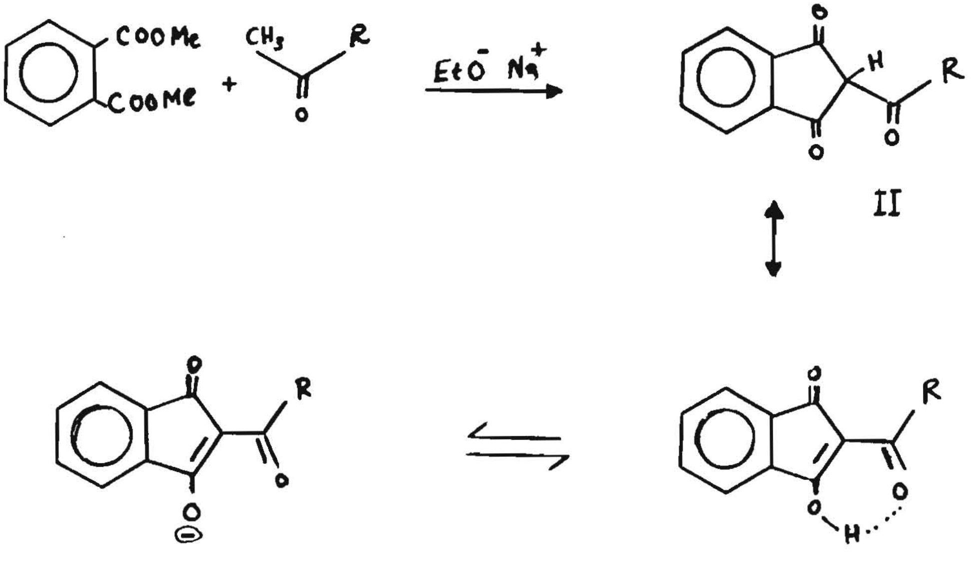
The compounds prepared and studied in this communication are shown below:

	R	Name
IIa	$-CH_3$	2-Acetyl-1,3-Indanedione (AID)
IIb	$-C_2H_5$	2-Propionyl-1,3-Indanedione (PID)
IIc	$-C_6H_5$	2-Benzol-1,3-Indanedione (BID)

Literature survey indicated that AID has been synthesized through two different synthetic routes, Sieglitz and Horn (1951) prepared AID by the condensation of vinyl acetate and phthalyl dichloride in presence of aluminum chloride while Merenyi and Nilsson (1964) obtained it through the condensation of 1-propen-2-yl acetate and phthalic anhydride in presence of aluminum chloride. However, a more generalized method was reported by Kilgore *et al.* (1942 which was modified by Horton and Murdock (1960).

The insecticidal properties of 2-acyl-1-3-indanedines have been studied by Kilogore *et al.* (1942) while their hypoprothrombinemic activity was investigated by Correll *et al.* (1952) and Heisey *et al.* (1956). Hassall (1950) studied the antibacterial properties of some analogues of 2-acyl-1, 3-indanediones.

The Kilgore *et al.* method, adopted in this study, involves the condensation of dimethylphthalate with the appropriate ketone in the presence of sodium ethoxide according to the following scheme.



II

IV

III

The vibrational absorption spectra of the compounds indicate the presence of both the keto structure (II) as well as the enol form (III). The OH stretching vibration due to intramolecular hydrogen bonding occurs as a broad band in the range 3100 — 2500 cm^{-1}. As the two forms contain different carbonyl groups, thus a number of bands occur in the range of 1800 — 1600 cm^{-1}. Fig. 1 shows the vibrational absorption of AID and BID (KBr pellet) in the range 2000 — 800 cm^{-1}. However, the PMR spectra show that the compounds exist exclusively in the enol form (III) in nonpolar solvent. The PMR spectral data of the compounds are summarized in Table 1. The PMR spectra of the compounds in $CDC1_3$ or $CC1_4$ have a highly downfield rather broad signal corresponding to one proton. This signal is due to the enolic -OH proton situated between two oxygen atoms *via* intramolecular hydrogen bonding as shown in structure III. Furthermore, upon the addition of D_2O, shaking and rerunning the PMR spectra, this highly down-field signal disappeared and another peak at S 4.5 ppm showed up due to the resulting HOD. The PMR spectrum of PID is shown in Fig. 2.

The electronic absortion spectrum of each form was obtained by the choice of the proper solvents. Ethanol, cyclohexane and 0.1 *N* NaOH media were used to obtain the spectra of the keto form (II), enol form (III) and enolate (IV) respectively. Table 2 summarizes the spectral data of the three compunds in the three media. The spectra of AID and PID are almost similar. On the other hand, the spectra of BID in the three media exhibit bathochromic shift as indicated in Table 2. This may be due to the presence of the phenyl group which incrcases the extent of conjugation of the chromophore group present in the compounds. It should be pointed out that spectra of the keto form (II) in ethanol and the enol form (III) in cyclohexane, of the three derivatives, are similar as far as the position of the absorption peaks but their corresponding molar absorptivities differ.

Table 1. PMR spectral data of the compounds

Compound	**Chemical shift (δ) ppm***		**Multiplicity**	**No. of protons**	**Assingment**
	$CDCl_3$	CCl_4			
AID					methyl group
					aromatic protons
	12.80**	13.30**	broad signal	1	chelated –OH proton
PID	1.33	1.35	triplet	3	$-CH_3$ of ethyl group
	3.05	3.01	quartet	2	$-CH_2-$ of ethyl group
	7.70	7.70	multiplet with sharp fine doublet	4	aromatic protons
	12.76**	12.71**	broad signal	1	chelated –OH proton
BID	7.20-8.20	7.20-8.50	multiplets	9	4 aromatic protons of the indanedione ring 5 aromatic protons of the phenyl group
	14.56**	15.00**	broad signal	1	chelated —OH proton

*Measured against TMS

**Signal disappears upon shaking with D_2O and another signal appears in the range 4.0 — 5.0 ppm due to HOD.

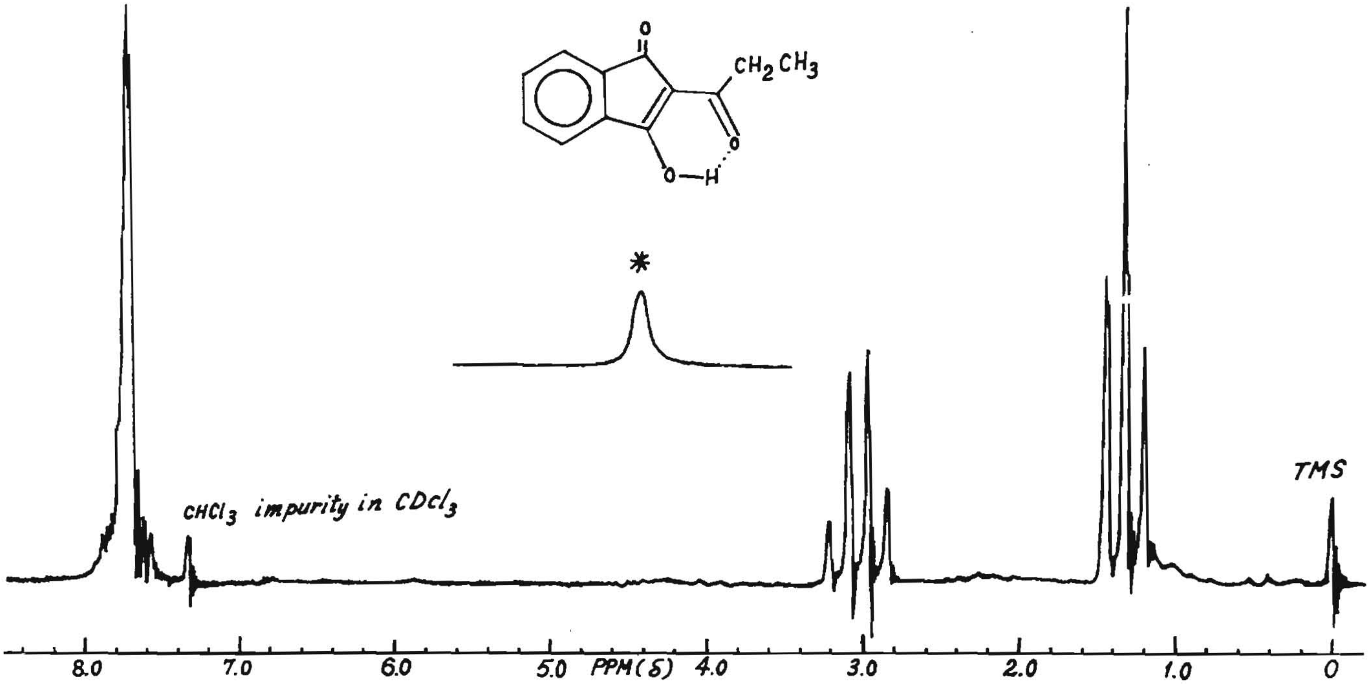


Fig. 1 : Vibrational absorption spectra of AID and BID (KBr pellets).

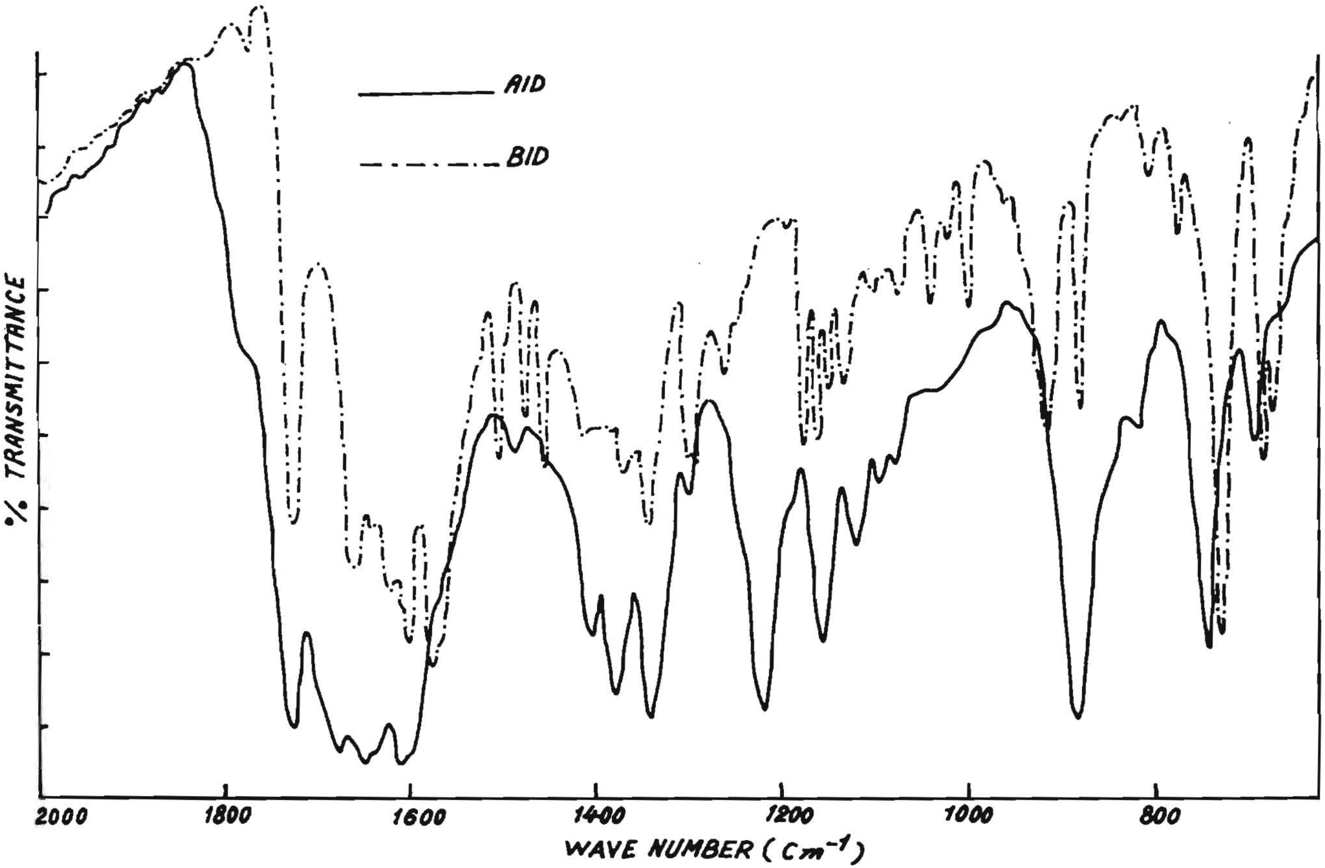


Fig. 2 : PMR spectrum of PID, Solvent: CDCl$_3$ internal standards: TMS.

*** This peak disappears when D$_2$O is added and another peak at about 4.5 ppm shows up (HOD peak)**

Table 2. Electronic absorption spectral data of the compounds.

Compound / Medium	AID		PID		BID	
	λ (nm)	ε	λ (nm)	ε	λ (nm)	ε
Ethanol (Keto form)	—	—	—	—	230	2.68×10^{4}
	236	2.95×10^{4}	237	3.05×10^{4}	240	2.75×10^{4}
	273	2.56×10^{4}	272	2.61×10^{4}	300	1.90×10^{4}
	282	3.25×10^{4}	283	3.31×10^{4}	—	—
	300	1.09×10^{4}	300	1.13×10^{4}	333	2.30×10^{4}
	308 (shoulder)	1.03×10^{4}	312 (shoulder)	1.01×10^{4}	—	—
Cyclohexane (Enol form)	—	—	—	—	231	2.28×10^{4}
	234	3.25×10^{4}	236	3.11×10^{4}	240	2.25×10^{4}
	271	2.31×10^{4}	272	3.64×10^{4}	300	1.75×10^{4}
	282	2.97×10^{4}	283	2.81×10^{4}	—	—
	300	1.13×10^{4}	300	1.11×10^{4}	334	2.35×10^{4}
	310	0.99×10^{4}	311	1.03×10^{4}	—	—
0.1*N* NaOH (Enolate)	—	—	—	—	231	3.50×10^{4}
	226	1.62×10^{4}	226	2.04×10^{4}	246 (shoulder)	2.50×10^{4}
	250	1.20×10^{4}	249	1.47×10^{4}	290	1.95×10^{4}
	282	3.06×10^{4}	282	3.54×10^{4}	—	—
	309	0.90×10^{4}	310	1.13×10^{4}	328	1.65×10^{4}
	321	0.86×10^{4}	322	1.09×10^{4}	—	—

* ε molar absorptivity.

The relative acidic strength of the compounds were quantitatively assessed by determining the pKa of each compound. This was achieved, in this study, by the potentiometric method developed by Albert and Serjeant (1971). The pKa values of the compounds were evaluated in 95% ethanol (Table 3). These values are concordant with the relative electronic effects of the different substituent group R in the compounds.

Table 3. The pKa values of the compounds.

Compound	pKa
AID	4.82 ± 0.05
PID	5.02 ± 0.04
BID	4.53 ± 0.05

Solvent: 95% ethanol. titrant : 0.1 *M* NaOH aqueous solution.

Preliminary investigation indicates that those compounds give highly colored metal chelates with Cu (II), Co (II), Ni (II) and Fe (III). The quantitative assessment of the chelating properties of such compounds and the study of their potential applicabilities in the determination of metal ions are the subject of further investigation.

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الخواص المخلبية للمركبات ٢ ـ آسيل ـ ١ و ٣ ـ إنديندايون

الجزء الأول : طرق التحضير والخواص الفيزيوكيميائية

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تم فى هذا البحث تحضير بعض مركبات ٢ ـ آسيل ـ ١ و ٣ ـ إنديندايون وذلك لدراسة خواصها المخلبية نحو عدد من المعادن الانتقالية وكذلك دراسة إمكانية استخدام هذه المركبات ككواشف للتعيين الكمى لهذه المعادن ٠ وتم تحضير هذه المركبات بتكثيف ثنائى ميثيل الفثلات مع الكيتون المناسب فى وجود أيون الأيثوكسيد وكذلك ثم تعيين الخواص الفيزيوكيميائية للمركبات المحضرة ٠٠ وهذه الخواص تشمل دراسة طيف الامتصاص فى منطقة الأشعة الفوق بنفسجية والأشعة دون الحمراء وكذلك طيف التردد النووى المغناطيسى كما تم تعيين قيمة ثوابت الحمضية بطريقة قياس الجهد ٠