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CHELATING TENDENCIES OF SOME SUBSTITUTED 2-(PYRIDYL)-1,3-INDANEDIONES WITH BIVALENT-METAL IONS

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Abstract—The acid dissociation constants of six substituted 2-(pyridyl)- and 2-(quinolyl)-1,3-indanediones and formation constants of three of these with some bivalent-metal ions have been determined at 30° in a 75 per cent (v/v) dioxane-water solution. The influence of steric, solvent, and electronic effects on the values of the formation constants is considered. Evidence is presented that suggests that solvent or electronic effects are responsible for the variations of chelating tendencies.

ALTHOUGH the chelating tendencies of substituted 2 picolyl ketones(1) ($2\text{-}C_5H_5NCH_2COR$) have been indicated, and those of β-ketoimines(2) have been determined, the chelating tendencies of the related 2-(pyridyl)-1,3-indanediones have not been measured. Substituted 2-(pyridyl)-1,3-indanediones have been of industrial interest because of the ability to form dyes.(3–5)

The present interest in the substituted 2-(pyridyl)-1,3-indanediones was occasioned by the relation of these compounds to the previously studied(2) β-ketoimines; both series of compounds possess the grouping —N═C—CH(R)CO—R′. While many of the β-ketoimines are susceptible to hydrolysis(2) the substituted 2-(pyridyl)-1.3-indanediones are resistant to hydrolysis under the conditions studied.

EXPERIMENTAL

Preparation of ligands (*Table 1*)

2,2-(Quinolyl)-1,3-indanedione (I) and *2-(3-hydroxy-2-quinolyl)-1,3-indanedione* (V) were obtained from The Koppers Company through the courtesy of Dr. W. C. FERNELIUS. The compounds were recrystallized prior to use.

Unless otherwise noted the other substituted 2-(pyridyl)-1,3-indanediones were prepared by refluxing a 1:1 molar ratio of phthalic anhydride and appropriately substituted 2-methylpyridine. A reaction period of 1–3 hr was sufficient. The crude product was recrystallized from a suitable solvent. The preparation of the following compound represents a typical synthesis—2-(*6-methyl-2-pyridyl*)-1,3-*indanedione* (III). A mixture of 2,6-dimethylpyridine (10·72 g., 0·1 mole) and phthalic anhydride (14·81 g., 0·1 mole) was refluxed for 1·5 hr. The product crystallized from benzene as orange crystals, m.p. 215–216°C.

Attempts were made to effect condensation of both methyl groups by using 0·2 mole of phthalic anhydride. A somewhat better yield of purified material (m.p. 215–218°C., 34 per cent) was obtained, but only the mono-condensation product was isolated. (Found: C, 74·55; H, 5·09; N, 5·90. Calc. for $C_{23}H_{12}O_4N$ (dicondensation): C, 75·20; H, 3·57; N, 3·81. Calc. for $C_{15}H_{11}O_2N$ (monocondensation): C, 75·94; H, 4·67; N, 5·90%.)

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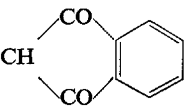
(2) D. F. MARTIN, G. A. JANUSONIS and B. B. MARTIN, *J. Amer. Chem. Soc.* **83**, 73 (1961).

(3) D. M. BROTHERS, *J. Assoc. Office Agr. Chemists*, **34**, 407 (1951).

(4) J. OGILVIE, U.S. Pat. **1**, 963 374, *Chem. Abstr.* **28**, 5251 (1932).

(5) Cf. *Chem. Abstr.* **30**, 4694 (1934).

TABLE 1.—PHYSICAL PROPERTIES OF SUBSTITUTED 2-(PYRIDYL)-1,3-INDANEDIONES, ArCH



Compound	Ar	Z	m.p. (°C)	Recryst solvent*	Yield (%)	Carbon (%)		Hydrogen (%)		Nitrogen (%)	
						Calc	Found†	Calc	Found	Calc	Found
I	2-Quinolyl	H	239–41	A	86	79·11	79·07	4·06	4·08	5·13	5·11
II	2-Pyridyl	H	286–88	A	83	75·33	75·10	4·06	4·12	6·28	6·41
III	6-Methyl-2-pyridyl	H	215–16	A	26	75·94	75·39	4·67	4·61	5·90	5·94
IV	2-Pyridyl	O_2N	325–26	B, C	33	62·69	62·38	3·01	2·77	10·44	10·23
V	3-Hydroxy-2-quinolyl	H	264–65	D	92	74·73	74·39	3·83	3·96	4·84	4·58
VI	3-Isoquinolyl	H	344–46	E + F, D	8	79·11	78·96	4·06	4·29	5·13	5·14

* A, benzene; B, 95 per cent ethanol; C, acetone; D, dioxane; E, glacial acetic acid; F, water.

† Microanalyses were carried out under the direction of Mr. Josef Nemeth at the University of Illinois.

2-(3-Isoquinolyl)-1,3-indanedione (VI). This compound was prepared using a method similar to one described by Phillips and Gross.(6) A mixture of phthalic anhydride (18·0 g, 0·12 mole), 3-methylisoquinoline (14·3 g, 0·1 mole) and zinc chloride (5 g, 0·04 mole) was heated at 180–190°C for 5 hr. The reaction mixture which crystallized on standing, was dissolved in 75 ml of hot glacial acetic acid, and the mixture was warmed on a steam bath for 10 min. The product precipitated upon addition of an equal volume of water and it was collected by filtration. An analytical sample was obtained after several recrystallizations from acetic acid and from dioxane.

Potentiometric titrations

The titrations were performed as described previously,(7,8) using dioxane which was purified by distillation from sodium and which was redistilled from sodium immediately before use. A nitrogen atmosphere was maintained during the titrations.

Absorption spectra

Infra-red absorption spectra (Table 4) were obtained in potassium bromide disks with a Perkin-Elmer Model 21 recording infra-red spectrophotometer. Ultraviolet absorption spectra (Table 5) were obtained with an Applied Physics Corporation, Model 14M recording spectrophotometer. Spectral samples were obtained by diluting stock solutions containing approximately 10 mg of compound per 50 ml of chloroform.

CALCULATIONS

The equations pertinent to the calculation of molarity quotients have been presented by Goldberg.(8) The titration data were run on the IBM 7094-1401 Data Processing System,* using a programme developed by W. J. Randall. For each titration point, the computer calculated $\bar{n}$ and used only those values that were within the prescribed ranges, 0·3–0·7 and 1·3–1·7. If an appropriate $\bar{n}$ value was obtained, values for the molarity quotients(8) Q_1 and Q_2 were obtained by one of two methods. For the $N = 1$ case, i.e., the coordination of only one bidentate ligand, the computer solved the equation by a method similar to that of Block and McIntyre.(9) For the case $N = 2$, the system of linear equations generated by taking one value for $\bar{n}$ in both $\bar{n}$ regions involved was solved by using Gauss' method of reduction and back substitution.(10)

RESULTS AND DISCUSSION

Acid dissociation constants. The pK_D values for the 2-(pyridyl)-1,3-indanediones were measured as a function of mole fraction of dioxane(N_2) at 30°, and mathematical expressions for the linear pK_D–N_2 relationship are listed in Table 2. Also included are the ranges of N_2 for which the expressions are valid. Previous workers have observed that the pK_D values of β-diketones(11) deviate from linearity at lower values of N_2, and this has been attributed to changes in tautomeric equilibria. Such deviations were not observed for the 2-(pyridyl)-1,3-indanediones over the range of N_2 that were studied, but the range of N_2 was limited by the solubility of some of the compounds.

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* Operated by the Digital Computer Laboratory, University of Illinois and partially financed through a National Science Foundation Grant, NSFGP700.

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(7) L. G. Van Uitert *et al., J. Amer. Chem. Soc.* **75**, 457 (1953); **76**, 5887 (1954).

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(10) H. Margenau and G. H. Murphy, *The Mathematics of Chemistry and Physics*, p. 497. Van Nostrand, New York (1956).

(11) L. G. Van Uitert and C. G. Haas, W. C. Fernelius and B. E. Douglas, *J. Amer. Chem. Soc.* **75**, 455 (1953).

Table 2.—pK_D Equations for N_2 range*

p$K_D = aN_2 + b$

Compound number	a	b	Range of N_2 reliable
I	13·11	9·84	0·173—0·386
II	9·04	10·07	0·113—0·386
III	10·28	10·45	0·136—0·386
IV	11·47	8·77	0·217—0·440
V	9·45	10·16	0·386—0·440
VI	9·13	8·72	0·155—0·386

* Valid to ±0·02

The acidity of the 2-(pyridyl)-1,3-indanediones can be correlated with electronic effects. The lower acidity of 2-(6-methyl-2-pyridyl)-1,3-indanedione(III) relative to the unsubstituted compound(II) can be attributed to an inductive effect leading to increased electron density on the pyridyl group. The quinoline derivatives (I and V) are the least acidic compounds of the series. As would be expected, the presence of an electron-withdrawing nitro group on the indanedione nucleus causes compound IV to be the most acidic of the series.

The first dissociation constant of 3-hydroxyquinophthalone(V) has been determined though there is doubt as to which proton is lost. In 75 volume per cent dioxane, the pK_D for this compound is 13·79 as compared with 14·93 for the quinophthalone(I). The fact that the hydroxy compound is appreciably more acidic would be in accord with a contention that the proton that is lost arises from the phenolic group rather than from the enolic. Holst(12) assigned the titrable proton of

$$o\text{-}HOC_6H_4COCH_2COC_6H_5$$

to the β-diketone function. Among other considerations, the assignment was made on the basis of deviation from a linear pK_D–N_2 relationship; such a consideration was not possible for compound V because of the narrow range of solubility in dioxane-water mixtures.

Formation constants. The chelating tendencies of compounds I–III with some bivalent-metal ions are listed in Table 3. The titration systems produced an internal consistency of ±0·02 in the log at the 95 per cent confidence level, and, for all titrations except cobalt, log K_n values were reproducible to within ±0·02. The values for cobalt are reproducible to within ±0·15, despite the fact that a nitrogen atmosphere was maintained in the titration flask. Formation constant of metal derivatives of compound V were not determined because of the indication that the titratable proton is not the proton that is lost upon coordination with a metal ion. Compounds IV and VI were not sufficiently soluble in 75 volume per cent dioxane to permit the determination of formation constants.

Trends that have been observed for other coordination compounds have also been noted in this study. The usual order of stabilities is found: $UO_2^{2+} > Be^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+} > Mg^{2+}$.(13,14) There are deviations: for compound I, zinc(II) forms a more stable derivative than cobalt(II); for compound II, the stability of the

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(12) E. H. Holst, Doctoral Dissertation, The Pennsylvania State University (1955).

(13) H. Irving and H. Rossotti, *Acta Chem. Scand.* **10,** 72 (1956).

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beryllium and the uranyl compounds was lower than that of the copper(II) compound. In a general way, the stability of a metal derivative, expressed as log K_1, is proportional to the pK_D of the 2-(pyridyl)-1,3-indaneione; the copper(II) derivatives represent the major exception. The complexes of the 2-(pyridyl)-1,3-indanediones are somewhat less stable than the corresponding complexes of 2-benzoyl hydrindone, a related β-dikestone,(15) but the indanedione complexes are generally more stable than the β-ketoimine complexes of comparable acidity.(2)

TABLE 3.—FORMATION CONSTANTS (LOG K_n)* OF BIVALENT-METAL CHELATES OF SOME 2-(PYRIDYL)-1,3-INDANEDIONES IN 75 PER CENT DIOXANE (N_2 = 0·386) AT 30°

Compound	n	Cu	Be†	Ni	Mn	Zn	Mg	Co	Uo_2†
I	1	11·62‡	11·78	NL§	9·31	10·53	7·33	9·80	12·95
	2	4·75	ppp.	NL	ppt.	ppt.	ppt.	ppt.	12·07
II	1	12·89	10·96	10·60	8·06	9·64	6·36	9·80	11·76
	2	ppt.	10·75	10·09	7·68	9·34	5·27	9·60	10·61
III	1	10·48	11·89	ppt.	8·72	8·88	6·86	NL	12·54
	2	12·25	11·61	ppt.	ppt.	11·56	6·44	NL	11·58

* Log K_1 and Log K_2 for the reactions $Ch^- + M^{2+} \rightarrow MCh^+$ and $Ch^- + MCh^+ \rightarrow MCh_2$, respectively.

† These solutions were prepared as nitrates rather than perchlorates.

‡ At 95 per cent confidence limits values are accurate to ±0·02

§ Only negative logarithms could be calculated from this determination.

Some of the deviations that have been noted above deserve further consideration. In particular, the anomalous pK_D–log K variation for copper(II) complexes is noteworthy. One of the steric effects which have been considered previously(16) seems applicable here. F-strain would make it troublesome for a ligand to approach a monochelated species, MCh^+, and an anomalously large separation factor K_1/K_2 should be noted. This effect is consistent with the behaviour noted for the quinophthalone copper(II) compound. Such an explanation is not possible for the copper(II) derivatives of compounds II and III. It is possible that the 6-methyl group (compound III) serves to shield the region around the nitrogen metal bond. If so, the anomalously low separation factor for the copper(II) and for zinc(II) complexes can be understood. In addition, a steric consequences of copper coordinating square planar and zinc tetrahedrally are such that the separation factor would be more favourable for zinc. It will be necessary to determine the change in enthalpy values before a definite statement can be made.

Absorption spectra. The infra-red absorption bands of interest are listed in Table 4 and are grouped according to assignments suggested by BELLAMY.(17) All spectra are characterized by an absorption band of moderate intensity in the region 3420–3440 cm^{-1} which is attributed to O—H stretching associated with the enolic form. In general, two carbonyl bands are noted: One, ca. 1670 cm^{-1}, is ascribed to a

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(15) B. B. MARTIN and W. C. FERNELIUS, *J. Amer. Chem. Soc.* **81**, 2342 (1959).

(16) D. F. MARTIN and B. B. MARTIN, *Inorg. Chem.* **1**, 404 (1962).

(17) L. J. BELLAMY, *The Infra-red of Complex Molecules*, 2nd. Ed. Methuen, London (1958).

non-hydrogen bonded carbonyl; the second, ca. 1600 cm^{-1}, is ascribed to a modified enol-chelate bond.(17) This assignment is similar to that suggested for 1-hydroxyquinones which have two bands at 1680–1675 cm^{-1} (free carbonyl) and 1630–1622 cm^{-1} (perturbed carbonyl).

All of the ultraviolet absorption spectra (Table 5) have the high intensity *K*-type bands expected of the conjugated systems of ligands I–VI. The spectra resemble those of aromatic β-diketones. For example, the band centered around 295 mμ (compounds III, IV) is similar to that noted for benzoylacetone,(18) and the band is probably a composite benzenoid–enolate band.

TABLE 4.—INFRA-RED ABSORPTION SPECTRA OF 2-(PYRIDYL)-1,3-INDANEDIONES

Compound	Hydroxyl (cm^{-1})	Carbonyl (cm^{-1})
I	3430 *m**	1585 *vsb*
II	3440 *m*	1595 *s*
		1675 *s*
III	3430 *m*	1600 *vsb*
		1635 *vs*
		1665 *s*
IV	3430 *m*	1600 *s*
		1635 *sb*
		1670 *s*
V	3420 *m*	1595 *s*
		1650 *sb*
VI	3440 *m*	1650 *sb*
		1670 *sb*

* *m* = moderate, *w* = weak, *s* = strong, *vs* = very strong, *b* = broad.

TABLE 5.—ULTRA-VIOLET ABSORPTION SPECTRA OF 2-(PYRIDYL)-1,3-INDANEDIONES*

Compound	M × 10^5	λ (mμ)	log ε_{max}
I	19·3	417	3·26
		443	3·25
II	9·68	395	3·38
		300	3·33
III	1·21	396	4·19
		290	4·18
IV	4·62	398	4·15
		290	4·14
V	1·02	422	4·27
		446	4·35
VI	1·32	368	4·19
		274	4·17

* $CHCl_3$ solution

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(18) A. E. GILLAM and E. S. STERN, *An Introduction to Electronic Spectroscopy in Organic Chemistry*, pp. 223–229. Arnold, London (1954).

This band is noted in the spectra of the quinoline derivatives (I, V, VI). Probably this is due to a bathochromic shift of the enolate band as is noted for benzoylacetone dibenzoylmethane, and for bis(β-diketones).(19)

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(19) cf. D. F. MARTIN, M. SHAMMA and W. C. FERNELIUS, *J. Amer. Chem. Soc.* **80,** 5855 (1958).