# Characterization of Linear and Branched Bis-β-diketone Ligands

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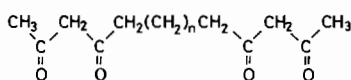*Department of Chemistry, Virginia Commonwealth University, 1001 W. Main Street, Richmond, Va. 23284, U.S.A.*

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## Abstract

Two series of tetraketones, consisting of two β-diketone moieties linked through alkyl chains to form either linear or branched structures, were investigated as the parent compounds of potentially bis-chelating, dinegative ligands for metal ions. The dependence of their keto-enol and acid-ionization equilibria on the point of attachment and length of the connecting alkyl chain was established by potentiometric titration and spectroscopic techniques (infrared, ultraviolet, $^1H$ and $^{13}C$ NMR).
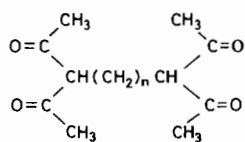
## Introduction

Bis-β-diketones ($LH_2$) of the general formulas **I** (linear) and **II** (branched) are the parent compounds of dinegative, tetradentate, bischelating ligands ($L^{2-}$). Their ability as coordinating agents was first recognized by Kluiber [1], Bailar [2], and Charles [3]. Two modes of coordination are possible for ligands of this type: (1) The two β-diketonato groups of each ligand may coordinate to separate

CH₃ CH₂ CH₂(CH₂)ₙCH₂ CH₂ CH₃ (structure)

n = 4, 6, 8

Type I ligands

(structure)

n = 6, 8, 10, 12

Type II Ligands

metal ions, resulting in ligand-bridged complexes which in turn may form either polynuclear chains or oligomeric rings. Polynuclear compounds of this type, $\{ML\}_n$, have been obtained for a number of

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divalent metal ions with several short-chain bis-β-diketonates [2, 3]. Two examples of cyclic dimers, $[M_2L_2]$, containing Be(II) at the coordination centers, have been described [1] for linear ligands with medium-length connecting chains. (2) The two β-diketonato groups of each ligand may coordinate to the same metal ion, resulting in a mononuclear 'bifurcate' complex with the connecting alkyl chain spanning across an edge or face of the coordinating polyhedron. Examples of this type of coordination have been reported for Be(II) with linear ligands in which the connecting chains were at least six atoms in length [1].

Other factors being equal, the mode of coordination of these bis-β-diketonato ligands to metal ions may be expected to depend on both the length and the point of attachment of the connecting alkyl chain. Short-chain branched ligands should strongly favor polynuclear coordination; short-chain linear ligands may give rise to either polynuclear chains or cyclic oligomers; linear and branched longer-chain ligands may loop to give bifurcate monomeric complexes. Compounds of the latter type should exhibit an increased stability compared to the analogous complexes of ordinary β-diketones, especially for those 2(+) and 4(+) metal ions in which the preferred coordination number is twice the ionic charge. Bifurcate complexes of bis-β-diketones may also be of interest because of the shielding effect and molecular dissymmetry arising from the presence of the spanning alkyl chain.

A systematic study of ligands of this type is of intrinsic value; it can also provide a useful background for the rational design of poly-β-diketones suitable for multiple chelation with the same metal ion. In this work we have considered the two series of linear and branched bis-β-diketones listed in Table I, in which the terminal groups were kept constant and the length of the connecting alkyl chain, $-(CH_2)_n-$, was varied from n = 4 to n = 8 for the linear compounds and from n = 6 to n = 12 for the branched analogs. These chain lengths were chosen because scale molecular models indicated that for shorter chains bifurcation would be virtually impossible, whereas for longer chains it might be somewhat less favorable owing to excessive flexibility.

TABLE I. Some Properties of Bis-β-diketones and Reference Compounds.

| Compound[a] and Abbreviation | 2,4-Pentane dione | Bis-β-diketone, O=⟨(CH₂)ₙ⟩=O | | | 3-Hexyl-2,4-pentane-dione | Branched bis-diketone, O=⟨(CH₂)ₙ⟩=O | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | n = 4, I-4 | n = 6, I-6 | n = 8, I-8 | | n = 6, II-6 | n = 8, II-8 | n = 10, II-10 | n = 12, II-12 |
| **M.P. (°C)** | [Liquid] | 68–69 | 71–74 | 78–81[b] | [Liquid] | 68–70 | 91–93 | 54–56 | 61–63 |
| Crystall. Solvent | | Methanol | Ethanol | Ethanol | | Benzene | Methanol | Methanol | Ethanol |
| **Infrared Absorptions[c] (cm⁻¹)** | | | | | | | | | |
| Carbonyl-Ketone | — | — | — | — | — | — | — | 1695 | 1690 |
| Enol-Chelate | | 1640–1600 | 1610 | 1640–1605 | — | 1605 | 1600 | — | — |
| **Ultraviolet Absorption[d]** | | | | | | | | | |
| Chloroform Solution | | | | | | | | | |
| $\lambda_{max}$ (nm) | 275 | — | 275 | — | | 293 | 293 | 293 | — |
| $\epsilon \times 10^{-3}$ | 11.0 ± 0.5 | — | 19.0 ± 0.5 | — | | (5.2 ± 0.3) | (5.2 ± 0.3) | 5.2 ± 0.3 | — |
| **Methanol–water Solution** | | | | | | | | | |
| $\lambda_{max}$ (nm) | 275 | — | 275 | — | | 293 | 293 | 293 | — |
| $\epsilon \times 10^{-3}$ | 5.5 ± 0.2 | — | 13.0 ± 1 | — | | 1.2 ± 0.1 | 1.2 ± 0.1 | 2.6 ± 0.1 | — |
| **Enol Percentage[e] (±1)** | | | | | | | | | |
| Initial[f] | [79, liquid] | | >99 | >99 (100, solid) | 32 (33, liquid) | >99 (100, solid) | | >1 (0, solid) | |
| At Equilibrium | 84 | | 83[d] | 25 | 25 | 25 | | 25 | |

[a] Compounds gave correct C, H microanalyses. [b] M.P. = 74–76 °C for sample recrystallized from benzene. [c] Solid samples were examined as Nujol mulls. Carbonyl ketone absorptions were strong and sharp; enol-chelate bands were strong and broad. [d] Values refer to equilibrium conditions; concentrations: $10^{-3}$–$10^{-4}$ M; temperature, 24 ± 0.5 °C. Initial values in cyclohexane; linear compounds, $\lambda_{max} = 273$, $\epsilon = (22.0 \pm 0.5) \times 10^3$; compounds II-6 and II-8 = $\lambda_{max}\ 289$, $\epsilon = (17.5 \pm 0.5) \times 10^3$; compounds II-10 and II-12: $\lambda_{max}\ 294$, $\epsilon = (4.0 \pm 0.1) \times 10^3$. [e] In $CDCl_3$ solution, 0.6–1.0 M, at 34 ± 0.5 °C. Percentages for the linear compounds were calculated from the intensities of the —CH= and —CH₂— ¹H NMR signals; for the branched compound and the 3-hexyl-derivative, the enolic —OH and keto- —CH— were used in the comparisons. The equilibrium of II-4 was studied over a wide concentration range and was found to be independent of concentration.

## Experimental

### Starting Materials

Reagent-grade 2,4-pentanedione, 1-bromohexane, and the $\alpha,\omega$-dibromoalkanes (Aldrich and Fluka) were used without further purification. Spectrophotometric grade solvents were used for all spectral measurements.

### Preparation of Bis-β-Diketones

The linear compounds I-4, I-6, and I-8 were prepared according to Hauser *et al.* [4], and were obtained as white crystalline solids (yields, 60–80%). The melting points appeared to be dependent on the solvent of crystallization (see compound I-8 in Table I); this may account for the slightly different values reported in the literature [1, 4]. The branched compounds II-6, II-8, II-10, and II-12 were prepared according to Fernelius *et al.* [5], except that the extraction of the reaction mixture after acidification was carried out with chloroform rather than benzene, as in the original procedure. Evaporation of the chloroform extracts gave the products as oils which upon prolonged standing in a refrigerator formed white crystals. Solids II-8, II-10, and II-12 were filtered, washed with cold methanol, and recrystallized several times from methanol or ethanol. Solid II-6 was recrystallized from benzene. Overall yields, 30–40%.

Compounds II-8 and II-12 are described for the first time in this work; II-6 and II-10 were previously known [5]. In our preparation of II-6, we found no evidence for the reported existence of an $\alpha$-form (m.p. 45.2–45.4 °C) and $\beta$-form (m.p. 80–82 °C); our analytically and spectroscopically pure product, crystallized from methanol, had m.p. 68–70 °C. One of the previously reported forms was most likely an O-alkylated isomer. Mono-O-alkylated by-products of the type $(CH_3CO)_2CH(CH_2)_n{-}O{-}C(CH_3){=}CHCOCH_3$, having distinctive $^1H$ NMR spectra, were indeed isolated in appreciable amounts from the syntheses of compounds II-10 and II-12; the O-alkyl-derivatives separated as white crystals when the oily residues from the isolation of the bis-β-diketones were kept in a refrigerator for a prolonged time (one month or longer). [$^1H$ NMR in $CDCl_3$-TMS: $\delta$ 4.60 (s, 1H, vinylic=CH–); 2.58 (t, 2H, –OCH$_2$–); 2.20–2.15 (double s, 12H, –CH$_3$); 1.8 (broad s, 2H, –CH$_2$–CH(COCH$_3$)$_2$); 1.12 (broad s, –(CH$_2$)H$_{n-2}$)].

3-hexyl-2,4-pentanedione [6, 7] was prepared similarly to the branched bis-β-diketones and was obtained as a pale yellow liquid containing approximately 8% of the O-alkyl-isomer. This was removed by complexation with copper(II): a solution of the crude product in boiling ethanol was treated with an excess of copper(II) acetate dissolved in hot water. The gray crystals that formed were filtered off,

washed repeatedly with water and ethanol, and redissolved in a slight excess of cold 40% sulfuric acid. Extraction of the acidic solution with chloroform, followed by washing, drying, evaporation of the chloroform extracts, and recrystallization, gave the product in pure form (yield 60%).

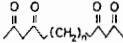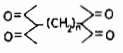### Characterization of the Compounds

Infrared spectra were obtained with a Perkin-Elmer Model 283 spectrophotometer. Solid compounds were examined as Nujol and hexachlorobutadiene mulls; 2,4-pentanedione and 3-hexyl-2,4-pentanedione were examined as liquids at room temperature and also as solids in Nujol after cooling by immersion in liquid nitrogen. The carbonyl stretching absorptions (1800–1500 cm$^{-1}$) are listed in Table I. Ultraviolet spectra were recorded on a Beckman Acta-M-VII spectrophotometer, with the cell compartment thermostated at $24 \pm 1$ °C. The absorption maxima and molar absorptivities of freshly prepared solutions (in cyclohexane) and of solutions at the tautomeric equilibrium (in chloroform and in a 80–20 volume–volume methanol–water mixture) are reported in Table I.

Fully decoupled $^{13}C$ NMR spectra were recorded in CDCl$_3$ solutions using a JEOL FX-90Q Spectrometer in the FT pulse mode at 22.50 MHz. For the linear compounds, the peak at $\delta$ 201.9 ppm could be revealed only with a scale expansion. Relevant $^{13}C$ data are summarized in Table II.

$^1H$ NMR Spectra were recorded in CDCl$_3$ solutions using a JEOL FX-90Q spectrometer for the assignment of the chemical shifts (Table II) and a Varian T-60 spectrometer for the quantitative study of the keto-enol equilibria (Table I). In the latter study, spectra were first recorded on freshly prepared solutions (concentration range, 0.6–1.0 M) and then again at regular intervals over a period of days, until a constant integration was obtained for the keto and enol resonance peaks. Samples were allowed to equilibrate at the temperature of the probe (34 °C) for about twenty minutes before recording the integration and several successive integrations were performed. For compounds I-4, the equilibrium was also investigated at lower concentrations (0.3, 0.2, 0.09, 0.03, 0.004 mol/l). In general, freshly prepared solutions showed only the $^1H$ NMR peaks of the tautomer present in the original solid; the peaks of the partner tautomer then appeared and gradually increased to equilibrium values. The time required to attain equilibrium ranged from 2–3 days for the linear compounds to 2 weeks for the branched compounds.

pH Titrations were performed in a covered vessel thermostated at $25 \pm 0.5$ °C, using a combination glass electrode and Corning Model 130 Digital pH Meter. All solutions were made up to have a 80–20 methanol–water volume ratio, using spectroscopic

TABLE II. Proton and Carbon-13 NMR Chemical Shifts[a] of Bis-$\beta$-diketones and Reference Compounds.

| Compound | 2,4-Pentanedione | (CH₂)ₙ bis-diketone<br>n = 4,6,8 | 3-Hexyl-2,4-pentanedione | branched<br>n = 6,8,10,12 |
|---|---|---|---|---|
| **$^1$H Spectra** | | | | |
| OH | 15.37s,br | 15.46s | 16.67s | 16.66s |
| $-CH=$ | 5.51s | 5.49s | − | − |
| $-COCH_2CO-$ | 3.60s | 3.58s | − | − |
| $-CH_3$(keto-) | 2.22s | 2.26s | 2.17s | 2.17s |
| $-CH_3$(enol) | 2.05s | 2.05s | 2.13s | 2.13s |
| $-CH_2COCH_2COCH_3$ | − | 2.50t | − | − |
| $-CH_2COCHCHOHCH_3$ | − | 2.27t | − | − |
| $-CO-\overset{\mid}{C}H-CO-$ | − | − | 3.61t | 3.61t |
| $-CH_2-CH(COCH_3)_2$ | − | − | 1.9−1.8m | 1.9−1.8m |
| **$^{13}$C Spectra[b]** | | | | |
| $\overset{\mid}{C}=O$ | 201.8 | 201.9 ($-CO-CH_3$)<br>204.0 ($-CO-CH_2-$) | 204.4 | 204.4 |
| $\overset{\mid}{C}-OH$ | 191.0 | 191.2 ($-COHCH_3$)<br>194.2 ($-COHCH_2$) | 190.8 | 190.7 |
| $-\overset{\mid}{C}=$ | 100.2 | 99.6 | 110.6 | 110.6 |
| $-\overset{\mid}{C}H$ | 58.4 | 57.9 | 69.1 | 69.1 |
| $CH_3-\overset{\mid}{C}=O$ | 30.6 | 30.7 | 29.3 | 29.2 |
| $CH_3-\overset{\mid}{\underset{\parallel}{C}}-OH$ | 24.6 | 24.8 | 27.6 | 27.6 |

[a]Chemical shifts are given as (ppm) relative to TMS (s = singlet, t = triplet, m = multiplet, br = broad). Measurements were carried out in CDCl$_3$ solution.    [b]At 22.50 MHz.

grade methanol and freshly boiled distilled water. The titrant was perchloric acid (*ca.* 0.1 M), prepared from 70% acid (Baker Reagent Grade) by dilution with methanol and water in the required ratio and standardized against 0.400 M sodium hydroxide. Samples were prepared by mixing 0.50 mmol of bis-$\beta$-diketone, 10 mmol NaClO$_4$, and 100 ml of methanol–water (80–20 v/v) in the titration vessel under a nitrogen atmosphere. After the resulting clear solution had attained a constant temperature, perchloric acid was added from a closed-system buret, stirring after each addition but not during the pH readings. The solution remained clear throughout the titration for all compounds except **II-12**, which began to precipitate at pH 11. The p$K_a$ values (reliable to 0.1 and 0.2 units for the linear and branched compounds, respectively) were obtained directly from the half-neutralization points of the titration curves.

## Results and Discussion

### Infrared Spectra

$\beta$-Diketones examined as pure liquids or in solution usually exhibit two very strong absorptions between 1700 and 1500 cm$^{-1}$. A sharp, often split, band near 1700 cm$^{-1}$ is typical of the keto-form, whereas a broader band near 1600 cm$^{-1}$ characterizes the 'enol-chelate' coexisting at equilibrium [8]. The infrared spectra of our crystalline bis-$\beta$-diketones showed instead the presence of one tautomer only (Table I). The linear compounds (**I-4, I-6, I-8**) and the shorter-chain branched compounds (**II-6, II-8**) were enols; the longer-chain branched analogs (**II-10, II-12**) were ketones. These findings contrast with previous reports, which suggested the presence of both a keto- and an enol-form in several crystalline bis-$\beta$-diketones [5] related to those investigated by us. To clarify this point, we examined the infrared spectra of several solid mono-$\beta$-diketones and found that 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, and 1,3-bis(3-pyridyl)-1,3-propanedione exhibited only the strong enol band at *ca.* 1600 cm$^{-1}$. A similar result was obtained for 2,4pentanedione examined as a solid at low temperature. It may be concluded that in the crystalline state a $\beta$-diketone generally consists of only one of the two forms present at equilibrium in the liquid phase; this is not surprising since the keto- and enol- forms have different

packing requirements and therefore are not likely to co-crystallize.

## $^{13}C$ and $^{1}H$ NMR Spectra. Analysis of the Keto-enol Equilibrium

The relevant carbon-13 and proton NMR data, with their respective assignments, are summarized in Table II. It may be noted that the enolic −OH proton of the branched bis-β-diketones and 3-hexyl-2,4-pentanedione are markedly shifted downfield ($\Delta$ = +1.30 ppm) compared to 2,4-pentanedione; a much smaller shift ($\Delta$ = +0.10 ppm) was observed for the linear compounds. In the equilibrium studies, the keto-enol percentages of the linear compounds and 2,4-pentanedione were determined from the relative intensities of the −CH− ($\delta$, 5.50) and −CH$_2$− ($\delta$, 3.60) signals. For the branched bis-β-diketones and the 3-hexyl-derivative, the central −CH− of the keto-form ($\delta$ 3.61) was compared with the enolic −OH ($\delta$, 16.67), which in these compounds appears as a sharp peak. The results of this analysis are summarized in Table I.

## Ultraviolet Absorption Spectra

All spectra (Table I) consisted of a fairly symmetrical absorption, centered at 273−275 and 293 nm for the linear and branched compounds, respectively. The intensity of the absorption, which in freshly prepared cyclohexane solutions ranged from $\epsilon = 2.2 \times 10^4$ for the linear compounds (*ca.* 100% enol) to $\epsilon = 4.0 \times 10^2$ for the branched compounds II-10 and I-12 (*ca.* 100% ketone), may be used to estimate the composition of each keto−enol mixture. The values thus obtained agreed well with those derived from $^{1}H$ NMR spectra.

## Acid-Base Properties

Potentiometric titration of the disodium salts of the bis-β-diketones in methanol−water solution, using dilute perchloric acid as the titrant, gave curves typical of very weak acids; a single sharp end point was observed at two mole-equivalent of titrant. The two β-diketone moieties thus ionized independently, their intramolecular interaction being hindered by the length of the connecting alkyl chain. The apparent 'p$K_a$' values obtained from the titration curves are given in Table I; they compare quite well with those of related mono-β-diketones under the same conditions. The small decrease in acidity from 2,4-pentanedione to the linear bis-β-diketones may be attributed to the electron releasing character of the connecting (terminal) alkyl chain; a similar but much more pronounced effect is observed in the 3-hexyl-derivative and the branched bis-β-diketones.

## Conclusions

This work provides a previously missing characterization for the two related series of bis-β-diketones parent ligands, **I** and **II**; it also provides a systematic correlation between their structures and their spectral and acid-base properties.

In general, both linear and branched bis-β-diketones closely resemble the corresponding mono-β-diketones, once the increase in molecular mass and the electronic effect of the connecting alkyl chain are taken into account. The effect of the alkyl chain depends markedly on the point of attachment: when this is a terminal C atom, only very minor changes in the $^{1}H$ NMR chemical shifts and in the keto-enol or acid-base equilibria are observed, compared to 2,4-pentanedione. When the point of attachment is the central C atom, however, a marked downfield shift of the enolic −OH proton results, together with a decrease of the enol percentage from 84% to 25% and a lowering of the acidity by a factor of nearly $10^2$. Linear and branched bis-β-diketonates may therefore be expected to exhibit rather different coordinating properties toward metal ions, the branched compounds being by far the weaker ligands.

These results contribute to rationalize a variety of unrelated observation available in the literature for mono-β-diketones. In regard to the keto-enol equilibrium, the presence of an electron-withdrawing substituent on the central C atom has been reported [9] to increase the enol percentage compared to 2,4-pentanedione itself. An electron-releasing alkyl chain should exert an opposite effect; this is consistent with the low enol content found for 3-hexyl-2,4-pentanedione and the branched bis-β-diketones. In regard to the $^{1}H$ NMR spectra, the enolic −OH resonance has been reported to occur at increasingly higher fields as the electron withdrawing character of the substituent increases [10]. The presence of an electron-releasing alkyl chain would then be expected to result in a downfield shift of the enolic −OH resonance relative to 2,4-pentanedione; such a shift is indeed observed for both the linear and the branched bis-β-diketones.

In general, any substituent that increases the electron density of the enol-chelate ring and thereby destabilizes the intramolecular hydrogen bonding of the enolic −OH will tend to reduce both the enol percentage and the acid strength. A parallel effect is usually observed for the $^{1}H$ NMR chemical shifts, an increased electron density of the enol-chelate ring resulting in a lower field resonance of the enolic proton. For some compounds, however, contrasting effects may come into play. In the examples of 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propane-dione, the strong electron-withdrawing character of the phenyl rings leads to nearly 100% enol

contents while their long-range deshielding effect causes the enolic −OH resonance to occur at unusually low field values [10]. An evaluation of substituent effects on the properties of β-diketone parent ligands, therefore, should distinguish between those electronic factors that relate specifically to NMR spectra and those which are chemically relevant and may result in changes of coordinating ability.

## Acknowledgement

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