α-Substituted β-diketones: effect of the α substituent on the complexation and selectivity for lanthanides †

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Some β-diketones having a substituent at the α position have been prepared and their keto–enol tautomerism, acid dissociation reaction and complexation with lanthanides have been studied. The tautomerism was examined by ^{1}H NMR spectroscopy, revealing that substitution of a methyl and bromo group at the α position of PhC(O)CH$_2$C(O)Ph or PhC(O)CH$_2$C(O)CF$_3$ decreases the percentage of the enol form drastically, whereas the parent diketones exist quantitatively in the enol form in CDCl$_3$. The pK_a value of PhC(O)CHMeC(O)CF$_3$ determined in 75% (v/v) 1,4-dioxane–water containing 0.1 mol dm^{-3} NMe$_4$ClO$_4$ at 25 °C was 10.36, being much larger than that of PhC(O)CH$_2$C(O)CF$_3$ (8.10). This weak acidity could be attributed to the strong intramolecular hydrogen bond which results upon decreasing the separation between the two donating oxygens through the steric repulsion between the α-methyl substituent and the terminal phenyl and trifluoromethyl groups. The diketone structures and the intramolecular hydrogen bond were evaluated using semiempirical molecular orbital calculations (MNDO/H), taking into account the hydrogen bond. The complexation with lanthanides has been examined *via* the solvent-extraction method. The lanthanides were extracted from a lower pH region with PhC(O)CH$_2$C(O)CF$_3$ than with PhC(O)CHMeC(O)CF$_3$ owing to its higher acidity. On the contrary, the separation with the latter was found to be better than that with the former. The separability is discussed with regard to the structures of the diketones.

β-Diketones are well known as versatile chelating reagents for metal ions. A large number of studies have been done especially in the field of solvent extraction of metal ions for the purpose of separation and concentration.[1,2] Much attention has been also paid to the structural chemistry of β-diketones involving keto–enol tautomerism and the intramolecular hydrogen bond.[3,4]
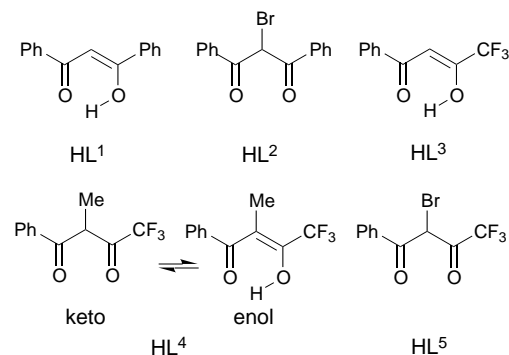
In the course of studies on the solvent extraction of metal ions with acylpyrazolones or acylisoxazolones, we noticed that improved extraction with strongly acidic extractants is usually accompanied by poor selectivity.[5–8] Examination of the ligand structure by molecular orbital calculations revealed a relationship among the separation of the two donating oxygens, the acidity of the ligands, and the extractability and separability of metal ions. In a previous paper,[9] trifluoroacetylcyclopentanone and -hexanone in which the separation of the two donating oxygens is controlled by the cyclic structure were prepared and a similar relationship as mentioned above was found.

In the present work, some α-substituted β-diketones have been prepared in the expectation that the distance between the donating oxygens could be controlled by the repulsion between the substituent at the α position and the terminal groups. The acid dissociation constants were measured by potentiometric titration, and the complexation with lanthanides was studied *via* the solvent-extraction method.

Experimental

Syntheses

2-Bromo-1,3-diphenylpropane-1,3-dione (HL^2). This compound was synthesized according to the literature[10] from dibenzoylmethane and *N*-bromosuccinimide. The crude white solid was recrystallized from methanol and dried *in vacuo* at 50 °C (67% yield), m.p. 89.4 °C. ^{1}H NMR (CDCl$_3$): δ 6.56 (s, 1 H, CHBr) and 7.40–8.05 (m, 10 H, C$_6$H$_5$) (Found: C, 59.6; H, 3.65. Calc. for C$_{15}$H$_{11}$BrO$_2$: C, 59.4, H, 3.65%).

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† *Non-SI unit employed:* cal = 4.184 J.

HL^1 HL^2 HL^3

keto ⇌ enol

HL^4 HL^5

2-Bromo-4,4,4-trifluoro-1-phenylbutane-1,3-dione (HL^5). A similar procedure was applied. The crude white solid was recrystallized from methanol and dried *in vacuo* at 30 °C (59% yield), m.p. 87.6 °C. ^{1}H NMR (CDCl$_3$): δ 5.40 (s, 1 H, CH) and 7.45–8.05 (m, 5 H, C$_6$H$_5$) (Found: C, 40.8; H, 2.1. Calc. for C$_{10}$H$_6$BrF$_3$O$_2$: C, 40.7; H, 2.05%).

4,4,4-Trifluoro-3-methyl-1-phenylbutane-1,3-dione (HL^4). This compound was synthesized according to the method of Barkley and Levine[11] through the condensation of methyl trifluoroacetate and propiophenone in the presence of sodium methoxide. The crude compound was purified by distillation followed by column chromatography (27% yield) (Found: C, 57.3; H, 3.95. Calc. for C$_{11}$H$_9$F$_3$O$_2$: C, 57.4; H, 3.95%). Further purification was *via* the copper salt method[11] to obtain the enol form. ^{1}H NMR (CDCl$_3$): keto, δ 1.54 [d, *J*(HH) = 7, 3 H, CH$_3$], 4.94 [q, *J*(HH) = 7, 1 H, CH] and 7.45–8.05 (m, 5 H, C$_6$H$_5$), enol, δ 2.05 [q, *J*(HF) = 2 Hz, 3 H, CH$_3$], 7.40–8.05 (m, 5 H, C$_6$H$_5$) and 15.81 (s, 1 H, OH).

Dibenzoylmethane (1,3-diphenylpropane-1,3-dione, HL^1) and 4,4,4-trifluoro-1-phenylbutane-1,3-dione (HL^3) (Dojindo) were reagent quality used without further purification. Other chemicals were all reagent-grade materials. Water was demineralized and distilled.

Apparatus

Metal-ion concentrations were measured with a Japan Jarrell Ash model ICAP-500 inductively coupled argon-plasma atomic emission spectrophotometer. The pH measurements were made with a Hitachi-Horiba F-8L pH-meter equipped with a Horiba 6028 glass combination pH electrode. The pH-meter was calibrated against standard reference buffers. Proton NMR spectra were measured with a Varian VXR-200 spectrometer (200 MHz) at 25 °C in CDCl₃. The extractions were performed in centrifuge tubes (30 cm³) with the aid of a type BR-30L Taitek Bio-shaker thermostatted at 25 °C. Semiempirical calculations and *ab initio* (RHF/3-21G) calculations were performed on fully optimized molecular geometries on a Cray Y-MP2E/264 computer using MNDO 94 (Cray Research Inc.) and GAUSSIAN 92.[12]

Measurement of acid dissociation constants (pK_a)

The pK_a values of HL[3] and HL[4] were determined according to the literature[13,14] by potentiometric titration. A 40 cm³ solution of 0.02 mol dm⁻³ diketone in water–1,4-dixoane (1:3 v/v) containing 0.1 mol dm⁻³ tetramethylammonium perchlorate kept in a thermostat at 25 °C was titrated by 0.1 mol dm⁻³ tetramethylammonium hydroxide solution.

Solvent extraction procedure

The concentration of the diketone was 0.1 mol dm⁻³ in benzene. Acetic acid or 2-morpholinoethanesulfonic acid monohydrate (mes) was used as buffering component. Standard metal salt solutions having concentrations of 0.01 mol dm⁻³ were prepared by dissolving their high-purity oxides (99.99–99.9999%) in hot concentrated nitric acid and diluted to give a 0.1 mol dm⁻³ nitric acid solution.

An aliquot (10 cm³) of an aqueous phase containing 1×10^{-4} mol dm⁻³ of lanthanide ion, 0.1 mol dm⁻³ sodium perchlorate and 0.01 mol dm⁻³ buffering component was adjusted to the desired pH with hydrochloric acid or sodium hydroxide solutions. The aqueous phase was shaken with an equal volume of benzene containing the required amount of diketone in a centrifuge tube (30 cm³) for 1 h at 25 °C. A shaking time of 1 h was found to be long enough for equilibration. After centrifugation the pH of the aqueous phase was measured and taken as the equilibrium value. The metal concentration in the aqueous phase was determined by inductively coupled plasma atomic emission spectrometry. That in the organic phase was measured in the same way after back extraction by stripping with 1 mol dm⁻³ hydrochloric acid solution. The sum of the metal concentrations in the two phases was in good agreement with the initial concentration.

Results and Discussion

Molecular orbital calculation

The distances between the two donating oxygens in the enol form of the β-diketones (bite size) were estimated by semiempirical MNDO/H[15] calculations which takes into account hydrogen bonding. Our semiempirical molecular orbital calculations including AM1[16] and PM3[17] show that MNDO/H is most suitable to evaluate the structure of β-diketones. Taking acetylacetone as an example, the O⋯O distance was found by X-ray and electron diffraction methods to be 2.54,[18] 2.52[19] and 2.51 Å,[20] respectively. Among those obtained by MNDO/H (2.50 Å), MNDO (3.05), AM1 (2.82) and PM3 (2.64 Å), that from MNDO/H is closest to the experimental value. The intramolecular hydrogen-bond energy (E_{OH}) can be estimated as the energy difference between the hydrogen-bonded structure and the open structure in which the O–H is rotated by 180° in order to minimize the hydrogen-bond energy. The value of E_{OH} from MNDO/H is 15.31 kcal mol⁻¹ which agrees well with the

Table 1 Structural data for HL[3] and HL[4]

	HL[3]	HL[4]
O⋯O [a]/Å		
HA	2.50	2.42
A⁻ [b]	3.09	2.78
E_{OH} [a]/kcal mol⁻¹	11.47	14.40
¹H NMR, δ(OH)	15.1 (br)	15.81 (sharp)
pK_a [c]	8.10 ± 0.02	10.36 ± 0.01

[a] From MNDO/H. [b] Fixed at planar. [c] Measured in 1,4-dioxane–water (3:1 v/v), 0.1 mol dm⁻³ NMe₄ClO₄.

value (14.38 kcal mol⁻¹) calculated using the equation postulated by Kopleva and Shigorin[21] taking the ν(O–H) frequency of 2750 cm⁻¹ assigned in the literature,[22] while those obtained by MNDO (6.23), AM1 (11.27) and PM3 (11.22 kcal mol⁻¹) are much smaller. Our results for other β-diketones also show that MNDO/H is the most appropriate. In addition, *ab initio* (RHF/3-21G)[12] calculations gave a value of 2.57 Å for acetylacetone.

Structure and keto–enol equilibrium of HL[1] and HL[2]

According to MNDO/H calculations, the bite size in the enol form of HL[1] is 2.51 Å. The introduction of one bromo group into the α position of HL[1] to give HL[2] reduces this bite size to 2.46 Å. The ¹H NMR spectrum of HL[1] in CDCl₃ shows one peak due to the α-methyne proton at δ 6.86 and the integral ratio for aliphatic hydrogen and aromatic hydrogen is about 1:10; moreover, there is a very broad peak due to the enolic proton at δ 16.2. It was reported that the hydrogen-bonded enolic proton signal appears at low magnetic field.[23] This signal did not move upon changing the concentration (0.01–0.1 mol dm⁻³) and disappeared after adding D₂O. From these facts, it can be deduced that HL[1] exists mostly in the enol form in CDCl₃. However, the ¹H NMR spectrum of HL[2] in CDCl₃ shows one peak due to the α-methyne proton at δ 6.56 with the integral ratio of the aliphatic hydrogen to aromatic hydrogen of about 1:10 and there is no OH peak from δ 8 to 30. This clearly suggests that HL[2] exists in its keto form in CDCl₃.

The solvent-extraction data for lanthanides into benzene also show that Yb, Ho and Eu can be quantitatively extracted with HL[1] at pH 8.1 while they are totally unextractable with HL[2], even when the pH was increased to 9.0. At pH > 9.0 hydrolysis of metal ions occurred leading to non-transparency of the aqueous phase. These results are in accord with those of Emsley[3] in the case of acetylacetone where introduction of a bromo group decreased the amount of the enol tautomer from 81 to 46%.

The presence of a bulky α-bromo group is expected to force the two carbonyl oxygens closer together thus strengthening the hydrogen bond between them and favouring the enol form, but at the same time there are also steric repulsions of the α-bromo group with the terminal phenyl groups. In order to prevent such interaction the keto form is preferred, which in this case is the more energetically stable.
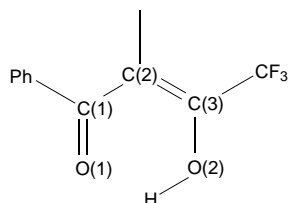
Structure and keto–enol equilibria of HL[3], HL[4] and HL[5]

In order to increase the percentage of the enol form, β-diketones with an electron-withdrawing substituent, which is expected to favour the enol tautomer,[24] have been examined. The compound HL[4], a derivative of HL[3], having an α-methyl group and an electron-withdrawing terminal substituent CF₃, was prepared; its O⋯O distance estimated by MNDO/H calculation is 2.42 Å compared to the 2.50 Å of HL[3] (Table 1). The MNDO/H optimized geometries of both compounds are summarized in Table 2. There is no significant difference in bond lengths in the enol skeleton except for O(1)⋯O(2) and consequently O(1)–H (Scheme 1). There are pronounced differ-

Table 2 Computed geometric parameters (distances in Å, angles in °) for HL³ and HL⁴*

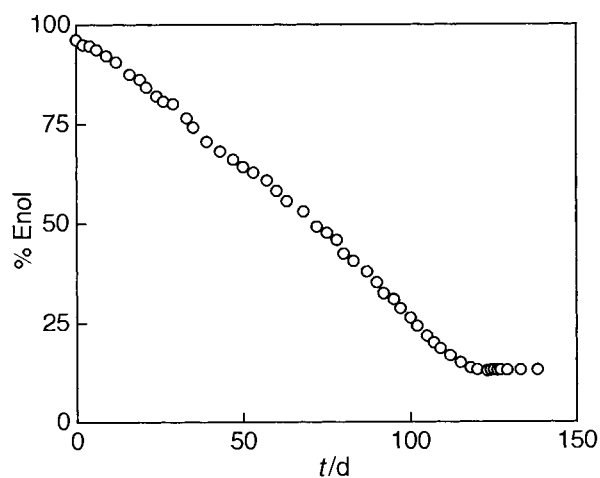|	HL³	HL⁴
C(1)–O(1)	1.24	1.24
C(1)–C(2)	1.49	1.51
C(2)–C(3)	1.37	1.38
C(3)–O(2)	1.34	1.34
O(2)–H	0.98	0.98
O(1)···H	1.68	1.59
O(1)···O(2)	2.50	2.42
O(1)–C(1)–C(2)	118.1	118.1
C(1)–(2)–C(3)	120.1	117.0
C(2)–C(3)–O(2)	122.8	122.9
C(3)–O(2)–H	111.8	112.7

* Calculated by MNDO/H.

Scheme 1

Fig. 1 Time dependence of the enol percentage

Fig. 2 Extraction of lanthanides into benzene with HL³ as a function of the pH of the aqueous phase. $[HA]_o = 0.1$ mol dm⁻³ in benzene, $[NaClO_4] = 0.1$ mol dm⁻³ in the aqueous phase

The ¹H NMR data show that the signal assigned to the hydroxyl proton of HL³ at δ 15.1 is very broad while that of HL⁴ is sharp at δ 15.81; these facts demonstrate that the intramolecular hydrogen bond of HL⁴ is stronger than that of HL³. The intramolecular hydrogen-bond energies calculated by MNDO/H are 11.47 and 14.40 kcal mol⁻¹ for HL³ and HL⁴ respectively, consistent with the ¹H NMR data.

An attempt was made to introduce Br into the α position of HL³, but similarly to the case of HL² and HL⁴ the HL⁵ obtained also exists mainly in the keto form, despite the presence of the CF₃ group which expected to increase the acidity and to favour the enol tautomer.

Acid dissociation constants of HL³ and HL⁴

All the pH measurements employed for determining pK_a were made in aqueous 1,4-dioxane, so the reading of the pH-meter was calibrated. Van Uitert and Hass[13] have demonstrated the validity of relationship (1) where B is the actual pH-meter

$$-\log [H^+] = B + \log U_H^0 + \log \gamma_\pm = B + \log U_H \quad (1)$$

reading, $\gamma_\pm$ the mean activity coefficient of HCl in the solvent mixture at the same temperature and ionic strength, and U_H^0 the correction to zero ionic strength. In this work the pH measurements were carried out at 25 °C with an ionic strength of 0.1 (NMe₄ClO₄) in water–1,4-dioxane (1:3) and the pH reading correction proposed by Irving and Mannot[14] has been adopted, equation (2).

$$-\log [H^+] = B + \log U_H = B + 0.28 \quad (2)$$

Least-squares fitting of the data sets comprising the amount of NMe₄OH solution added and the pH value to the acid–base titration curve[25] gave the pK_a values of HL³ and HL⁴ as 8.10 ± 0.02 and 10.36 ± 0.01, respectively. The difference could be attributed to the fact that the shorter O···O distance of HL⁴ strengthens the intramolecular hydrogen bond thus hinders the release of the proton, resulting in a decrease in acidity.

Solvent extraction of lanthanides with HL³ and HL⁴

The effect of the O···O distance of the diketones HL³ and HL⁴ on their complexation with metal ions has been investigated *via* the solvent-extraction method.[1,2,26] The solvent-extraction behaviours of lanthanides (Ln³⁺) from a 0.1 mol dm⁻³ sodium perchlorate aqueous phase to a 0.1 mol dm⁻³ HL³

ences in the bond angles C(1)–C(2)–C(3). The smaller bond angle for HL⁴ must be caused by steric repulsion between the α-CH₃ and the terminal Ph and CF₃ groups.

Compound HL⁴ after being purified by fractionated distillation and column chromatography exists mainly in the keto form: the amount estimated from the ratio between the integral of the CH₃ keto peak and the sum of the integrals of the CH₃ keto and enol peaks is 87%. On the other hand, when the ligand is purified by the copper salt method it exists mostly in the enol form (96%). This can be explained by a necessary transformation to the enol configuration that allows HL⁴ to form the copper complex. However, a time-dependent ¹H NMR investigation showed that the heights of the OH and CH₃ enol peaks decreased gradually whereas that of the CH₃ keto one increased. The time-dependent decrease in the peaks of the enol tautomer clearly shows that the keto tautomer is more stable in CDCl₃. The time dependence of the enol percentage is shown in Fig. 1. It takes more than 120 d for the percentage to reach the constant value (13%). The enol content did not change if the enol rich HL⁴ just after purification by the copper salt method was stored in a refrigerator at −18 °C. This sample was used for the pK_a measurement and the lanthanide extraction.
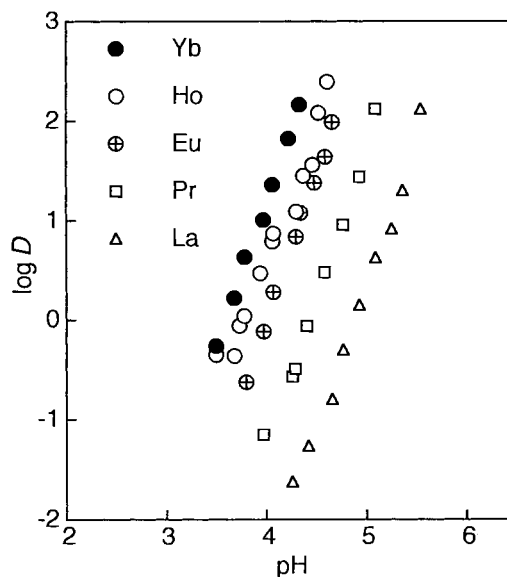
Table 3 Values of $pH_{1/2}$, the extraction constants and separation factors in the extraction of lanthanides with HL^3 or HL^4

	HL^3			HL^4		
Ion	$pH_{1/2}$ [a]	$\log K_{ex}$	s.f. [b]	$pH_{1/2}$ [a]	$\log K_{ex}$	s.f. [b]
La^{3+}	4.88 ± 0.02	-11.63 ± 0.05		6.81 ± 0.03	-17.42 ± 0.08	
			1.36 ± 0.06			1.58 ± 0.09
Pr^{3+}	4.42 ± 0.01	-10.27 ± 0.04		6.28 ± 0.01	-15.84 ± 0.04	
			1.25 ± 0.04			1.53 ± 0.04
Eu^{3+}	4.01 ± 0.01	-9.002 ± 0.02		5.77 ± 0.01	-14.31 ± 0.01	
			0.60 ± 0.08			0.71 ± 0.03
Ho^{3+}	3.81 ± 0.03	-8.42 ± 0.08		5.53 ± 0.01	-13.60 ± 0.03	
			0.61 ± 0.08			0.67 ± 0.04
Yb^{3+}	3.60 ± 0.01	-7.81 ± 0.02		5.31 ± 0.01	-12.93 ± 0.03	
			3.82 ± 0.05 [c]			4.49 ± 0.09 [c]

[a] Extraction into benzene. $[HL^3]_o = [HL^4]_o = 0.1$ mol dm^{-3}. [b] Separation factor defined by the difference in $\log K_{ex}$ values for two consecutive metals in this table. [c] Separation factor for La/Yb.

(HA) benzene phase are shown in Fig. 2, in which the logarithmic value of the distribution ratio of the metal ions, $\log D$ ($D = [Ln^{3+}]_o/[Ln^{3+}]$), is plotted against the pH of the aqueous phase, where the subscript o denotes the species in the organic phase. The plots are linear with slopes of *ca.* 3. In order to clarify the composition of the extracted species the effect of $[HA]_o$ on $\log D$ was also examined. The slopes of the straight lines were again *ca.* 3, indicating that the extracted species is LnA_3 and no adducts such as $LnA_3(HA)_n$ ($n = 1, 2, \ldots$) are observed. Based on these slope analyses, the extraction equilibrium can be expressed as in equation (3). The extraction

$$Ln^{3+} + 3HA(o) \rightleftharpoons LnA_3(o) + 3H^+ \quad (3)$$

constant, K_{ex}, is defined as in equations (4) and (5). The $\log K_{ex}$

$$K_{ex} = \frac{[LnA_3]_o[H^+]^3}{[Ln^{3+}][HA]_o^3} = D\frac{[H^+]^3}{[HA]_o^3} \quad (4)$$

$$\log K_{ex} = \log D - 3pH - 3\log[HA]_o \quad (5)$$

values were obtained by substituting the $pH_{1/2}$ values, *i.e.* the pH read from plots of $\log D$ *vs.* pH at the point where half of the metal ion is extracted ($\log D = 0$), in equation (5) and are summarized in Table 3. Since the concentration of the lanthanide ion is much smaller than that of the extractant, the concentration of the extractant in the organic phase {$[HA]_o$ in equation (5)} can be considered equal to the initial concentration.

The higher acidity of HL^3 than that of HL^4 leads to its considerably greater effectiveness in the extraction of lanthanides: the extraction constants for all the extracted metals are 10^5 to 10^6 times larger than those of HL^4, but it is also obvious that HL^4 with its smaller bite size is superior in discriminating between lanthanides. We define the separation factor (s.f.) between two metals as the difference between their $\log K_{ex}$ values; thus the s.f. between La and Yb with HL^4 is 4.49 (see Table 3), larger than that with HL^3 (3.82) and 4,4,4-trifluoro-1-(2-thienyl)butane-1,3-dione (3.79),[26] one of the most well known and typical β-diketones. Consequently, HL^4 can be considered as a highly selective extractant for lanthanides. This result once again verifies our recent observation[9] that the $O \cdots O$ distance is a significant factor in governing the acidity of the extractant and its selectivity for metal ions, in this case of lanthanides.

The extraction of metal ions is considered to involve removal of the diketone (HL^3 or HL^4) from the organic phase, becoming an anionic form in the aqueous phase, complexed with the metal ion (Ln^{3+}) followed by the redistribution of the complex into the organic phase.[1,2] The heat of formation (H_f) of the anionic species was obtained by MNDO/H calculation, varying the distance between the two donating oxygens. The β-
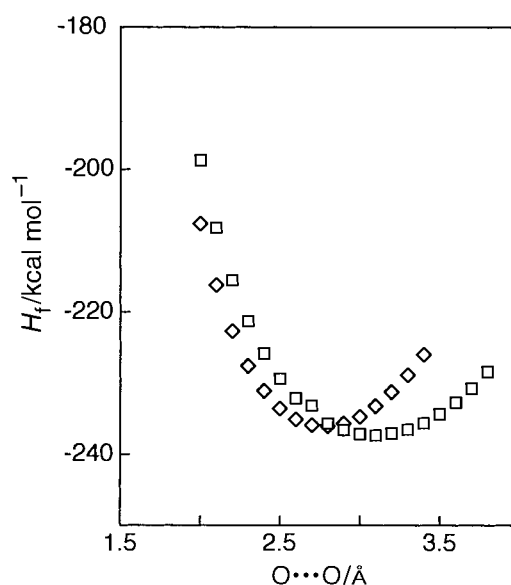

Fig. 3 Plots of the heat of formation (H_f) *vs.* the $O \cdots O$ distance for the anionic forms of HL^3 ($\square$) and HL^4 ($\diamond$), H_f was calculated by MNDO/H

diketone moiety including the two carbonyl groups and the carbon in the α position were fixed on a plane in the calculation, for the β-diketone moiety usually remains on the plane or is approximately coplanar in the lanthanide complexes. Plots of H_f *vs.* the $O \cdots O$ distance are seen in Fig. 3. The most stable conformation of the anionic form is obtained when the $O \cdots O$ distance is 3.09 Å for HL^3 and 2.78 Å for HL^4. It has been reported on the basis of X-ray crystallographic data that for lanthanide β-diketonates the $O \cdots O$ distance usually lies in the range 2.7–2.9 Å.[27–30] In the series of lanthanides the larger the atomic number the smaller is the ionic radius and consequently the larger the charge density, so in chelating extraction systems the metal ion with larger atomic number is more effectively extracted. Some amount of energy is needed for $[L^3]^-$ with its bite size of 3.09 Å to arrange its conformation to fit the complex structure and even more energy is required to complex smaller metal ions. This extra energy cancels the advantage in complexation brought about by the larger charge density of the smaller metal ions, resulting in a reduced selectivity. In the case of $[L^4]^-$ with a bite size of 2.78 Å not so much energy is required to complex smaller metal ions, thus the selectivity is less reduced or is even enhanced if extra energy is needed to complex larger metal ions.

Conclusion

It was shown that the $O \cdots O$ distance in β-diketones can be

controlled by introducing a substituent at the α position. The acidity and the keto–enol equilibrium is influenced drastically. It is most noteworthy that the reaction with metal ions, *i.e.* the extractability and separability for lanthanides, was affected by this modification; the separability for lanthanides is improved at shorter O⋯O distances as seen in our previous work.[9] This could provide a guide to improving the known ligands and suggest a novel strategy for the design of ligands having high selectivity.

Acknowledgements

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