Schiff Bases of Acetone Derivatives: Spectroscopic Properties and Physical Constants

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Summary. *Schiff* bases of acetylacetone, benzoylacetone, dibenzoylmethane, and thienoyltrifluoroacetone with ethanolamine and 2-aminophenol were synthesized and characterized by elemental analysis, infrared and ^{1}H NMR spectra. Dissociation constants of the synthesized ligands were determined in methanol-water and at an ionic strength of $0.1\,M$ KNO_3 at different temperatures; the associated thermodynamic parameters were calculated. Single crystals of one of the ligands were prepared; the X-ray diffraction pattern was analyzed. Thermal analyses of the investigated ligands were performed and correlated with the ligand structure.

Keywords. Acetylacetone; Benzoylacetone; Dibenzoylmethane; Thienoyltrifluoroacetone; Dissociation constant; Single crystals.

*Schiff*sche Basen von Acetonderivaten: Spektroskopische Eigenschaften und physikalische Konstanten

Zusammenfassung. *Schiff*sche Basen von Acetylaceton, Benzoylaceton, Dibenzoylmethan und Thienoyltrifluoroaceton mit Ethanolamin und 2-Aminophenol wurden hergestellt und mittels Elementaranalyse, IR-Spektroskopie und ^{1}H-NMR-Spektroskopie charakterisiert. Die Dissoziationskonstanten wurden in Ethanol-Wasser bei einer Ionenstärke von $0.1\,M$ KNO_3 bei verschiedenen Temperaturen bestimmt; die entsprechenden thermodynamischen Größen wurden berechnet. Das Röntgendiffraktionsmuster eines Einkristalls einer der Verbindungen wurde analysiert. Thermische Untersuchungen wurden durchgeführt und die Ergebnisse mit den Strukturen korreliert.

Introduction

β-Diketones have found immense analytical applications [1–4]. Several analogous compounds have been synthesized by the introduction of substituent groups in different positions for improved analytical characteristics. *Bertrand* and his coworkers [5] have reported the preparation of tetradentate *Schiff* base ligand by condensation of 2-aminoethanol with 2,4-pentanedione. It has been shown that the ligand contains three ionizable protons and can form neutral 1:1 complexes with trivalent metal ions. With divalent metal ions, only two protons are liberated from the ligand (one from the methylene group between the two $-C=N-$ groups and one

from the alcohol OH) forming neutral complexes. The remaining proton would be expected to participate in strong hydrogen bonding [6, 7]. Copper(II) complexes are binuclear, and their magnetic moments have shown a temperature dependent behaviour indicative of exchange coupling [8–11]. Also, there was a considerable interest in the tetrameric copper(II) complex [Cu(*acac*-ethanolamine)]$_4$ with unusual properties which contains pentacoordinate copper(II) [12, 13].

Schiff bases resulting from the condensation of benzoylacetone and ethanolamine or propanolamine have been used for the synthesis of copper(II) complexes [14]. Molecular weight determinations in chloroform indicate that [Cu(benzoylacetone-ethanolamine)]$_4$ is tetrameric with a positive *Weiss* constant θ. In addition, [Cu(benzoylacetone-propanolamine)]$_2$ is dimeric with a large negative value of the exchange integral and a singlet ground state [13].

The present article aims to a better understanding of the structure of these ligands. To achieve this goal, *Schiff* bases were synthesized by coupling of ethanolamine as well as aminophenol with dibenzoylmethane, benzoylacetone, acetylacetone, and thenoyltrifluoroacetone. The synthesized ligands were characterized using elemental analysis, infrared, and ^{1}H NMR spectra. The dissociation constants of the ligands were calculated potentiometrically at different temperatures, and the associated thermodynamic parameters were determined. Single crystals of one of the *Schiff* bases have been prepared using *TMOS* (tetramethoxy silane) as gelling agent. The crystal structure has been determined by X-ray analysis. The thermal properties of the synthesized ligands have been measured and are interpreted.

Results and Discussion

Ligand characterization

The purity of the synthesized *Schiff* bases was confirmed by chemical analysis, melting point (Table 1), and TLC (silica gel GF254 type 60, mesh size 50–250, eluted with ethanol-chloroform).

Infrared and ^{1}H NMR spectra

^{1}H NMR spectra of **A** type ligands (*DMSO*-d$_6$) showed the aromatic protons at $\delta = 6.22$–8 ppm (**A1**), 6.8–8 ppm (**A2**), and 6.72–7.11 ppm (**A3**). On the other hand, **A4** exhibited two groups of signals, the first at $\delta = 6.3$–6.5 ppm for 4H of the phenyl group, and the second at $\delta = 6.5$–6.8 ppm corresponding to 3H of the thiophene ring [18]. The OH proton of the enol resonates at $\delta = 10.10$ ppm (**Al**), 10.05 ppm (**A2**), and 9.95 ppm (**A3**). Since **A4** has no signals in this range, it is most likely to assume that the ligand prefers the keto form [19]. The OH proton on the phenyl ring appears as singlet at $\delta = 12.67$ ppm (**A1**), 12.89 ppm (**A2**), 12.17 ppm (**A3**), and 9.0 ppm (**A4**) [19]. The acidic protons of –CH$_2$–[–CH$_2$– $\leftrightarrow$ =CH–] resonate as singlet at $\delta = 6.2$ ppm (**A1**), 6.0 (**A2**), 5.19 ppm (**A3**), and 4.5 ppm (**A4**) [18–20]. The protons of the phenolic and enolic OH as well as those of the –CH$_2$– moiety are exchangeable with D$_2$O, and the HOD signals appear at $\delta = 3.95$ ppm (**A1**), 4.0 ppm (**A2**), 3.7 ppm (**A3**), and 4.3 ppm (**A4**) [18].

Table.1. Analytical data, effect of temeprature, and colours of the synthesized ligands

No.	Name	Formula	Mol.Wt.	Colour	Effect of temperature m.p.	decomp.p.	C (%) Found	Calcd.	H (%) Found	Calcd.	N (%) Found	Calcd.
1	**A1** $R_1 = R_2 = Ph$	$C_{21}H_{17}NO_2$	315.37	Orange	198	142	79.95	79.97	5.55	5.44	4.87	4.44
2	**A2** $R_1 = Ph, R_2 = CH_3$	$C_{16}H_{15}NO_2$	253.30	Yellow	167	145	75.10	75.86	5.95	5.98	6.05	5.53
3	**A3** $R_1 = R_2 = CH_3$	$C_{11}H_{13}NO_2$	191.23	Yellow	184	183	69.13	69.08	6.81	6.87	7.65	7.33
4	**A4** $R_1 =$ thiophenyl, $R_2 = CF_3$	$C_{14}H_{10}NO_2SF_3$	313.29	Golden-yellow	172	150	53.63	53.67	3.20	3.22	4.42	4.47
5	**B1** $R_1 = R_2 = Ph$	$C_{17}H_{17}NO_2$	267.33	Yellow	80	125	76.30	76.37	6.70	6.42	5.30	5.24
6	**B2** $R_1 = Ph, R_2 = CH_3$	$C_{12}H_{15}NO_2$	205.26	Yellow	88	170	70.60	70.21	7.43	7.38	6.96	6.83
7	**B3** $R_1 = R_2 = CH_3$	$C_7H_{13}NO_2$	143.18	Yellow	65	160	58.48	58.72	9.15	9.17	9.78	9.78
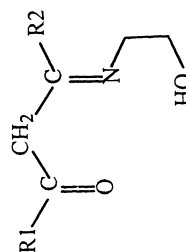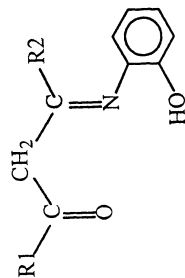
On the other hand, ^{1}H NMR studies of **B** type ligands (*DMSO*-d$_6$) showed triplets corresponding to –CH$_2$– of the ethanolamine moiety near the –OH resonance at $\delta = 2.7$ ppm (**B1**), 3.4 ppm (**B2**), and 3.3 ppm (**B3**), but the signals of the –CH$_2$– group near the azomethine nitrogen was obtained as a triplet at $\delta = 3.5$ ppm (**B1** and **B3**) and $\delta = 3.6$ ppm (**B2**) [21, 22]. The –OH protons (ethanolamine tail) resonate as singlets at $\delta = 5.85$ ppm (**B1**), 5.0 ppm (**B2**), and 4.8 ppm (**B3**). The –CH$_2$– $\leftrightarrow$ =CH– protons appear as singlets at $\delta = 6.9$ ppm (**B1**), 5.8 ppm (**B2**), and 5.0 ppm (**B3**) [20]. Finally, the enolic –OH protons resonate as singlets at $\delta = 11.5$ ppm (**B1**), 11.4 ppm (**B2**), and 10.7 ppm (**B3**) [19]. The 10-aromatic protons of **B1** are observed at $\delta = 7.5–8.0$ ppm, and the 5-aromatic protons of **B2** at 7.4–7.9 ppm. The –OH protons of the ethanolamine, the enol hydroxyl proton, and the CH– $\leftrightarrow$ =CH– protons are exchangeable with D$_2$O; very strong and sharp signals of HOD appear at $\delta = 4.0$ ppm (**B1**), 4.25 ppm (**B2**), and 4.4 ppm (**B3**).

IR spectra of **A1** and **A4** show a strong band at 3370 cm^{-1} which is assigned to ν_{OH} of the enol tautomer of the β-diketone moiety of the ligands [23]. Also, these ligands show sharp bands centered at 3310 and 3300 cm^{-1} which may be attributed to the phenolic OH. The strong broad bands around 3000 cm^{-1} in the IR spectra of **A2** and **A3** ligands may be attributed to intramolecular hydrogen bonding which is confirmed by the appearance of bands centered around 2710, 2720, 2700, and 2700 cm^{-1} for **A1**, **A2**, **A3**, and **A4**, respectively. For **B1**, **B2**, and **B3**, the –OH frequency was obtained at 3310, 3350, and 3270 cm^{-1}, respectively. Strong overlapping absorptions at 1600, 1560 cm^{-1} (**A1**), 1590, 1560 cm^{-1} (**A2**), 1600, 1540 cm^{-1} (**A3**), 1600, 1510 cm^{-1} (**A4**), 1590, 1550, 1530 cm^{-1} (**B1**), 1600, 1590, 1520 cm^{-1} (**B2**); and 1600, 1550 cm^{-1} (**B3**) are related to the double bond stretching modes [24, 25]. It has to be noted that the *Schiff* bases under consideration do not exhibit characteristic $>$C=O absorption bands (1720–1708 cm^{-1}) which indicate the enolic contents of these ligands.

Acid dissociation constants

The dissociation constants of **A** and **B** type *Schiff* base ligands were determined by titrating 50 cm^3 of the ligands (0.005–0.01 M) with 0.1 M KOH at a constant temperature of 15, 25, and $35 \pm 0.1°$C and an ionic strength of 0.1 M KNO$_3$ in methanol-water (10–60% v/v). A representative plot of the titration curves of the ligands is shown in Fig. 1. The protic nature of the ligands is substantiated from the titration curve:

(i) in case of **B** ligands, one proton is liberated as indicated by an inflection at $m = 1$;
(ii) for **A** ligands, two protons are ionized as shown by an inflection at $m = 2$ (*m*: number of moles of base per mole of ligand).

This indicates that the acid-base equilibria in the *pH* range of 5.4 to 12.5 based on the molecular forms LH (**B**) and LH$_2$ (**A**) in the potentiometric titrations are in accordance with the following equations:
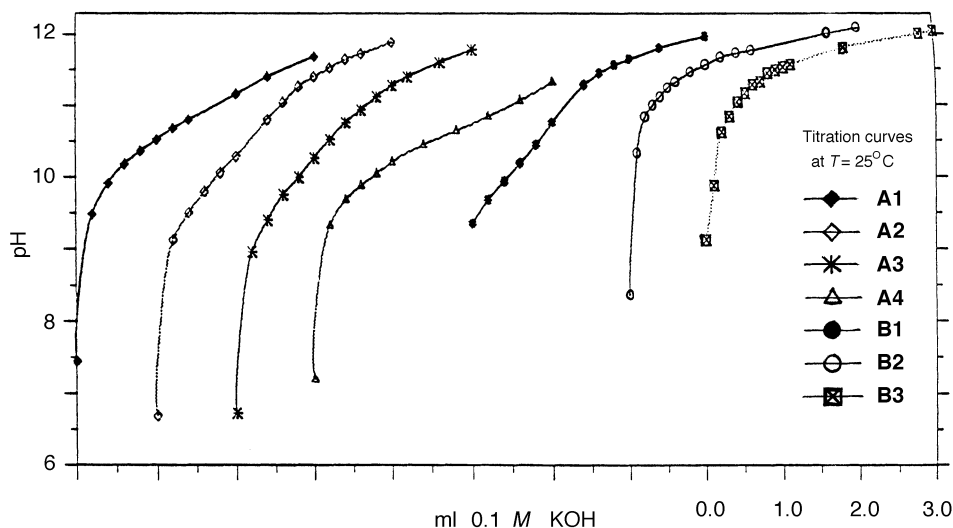
$$LH_2 \leftrightarrow LH^- + H^+ \quad pK^{AH}$$
$$LH^- \leftrightarrow L^{-2} + H^+ \quad pK^{AH}$$
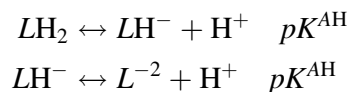
Fig. 1. *pH*-metric titration curves of the free ligands at 25°C; $V_0 = 50$ ml, $I = 0.1\,M$ KNO$_3$, [KOH] $= 0.1\,M$; [**A1**] $=$ [**A2**] $=$ [**A3**] $= 0.005\,M$ in 60% (v/v) methanol-water; [**A4**] $= 0.005\,M$ in 40% (v/v) methanol-water; [**B1**] $= 0.005\,M$ in 60% (v/v) methanol-water; [**B2**] $=$ [**B3**] $= 0.01\,M$ in 10% (v/v) methanol-water

The MINSQ non-linear least-square computer program [17] was used to calculate the dissociation constants (pK^H) and the species distribution diagrams. The program employs a least squares minimization procedure based on a modification of the *Levenberg-Marquadt* technique within the *pH* range determined by the lowest point of neutralization. The calculated values are shown Table 2. A satisfactory fit between the calculated parameters and the experimental data is indicated by reasonable values for the MINSQ objective functions.

A substituent on the organic chelating agent often changes the chelating ability in addition to changes of other chemical and physical properties. The acidities of **A** and **B** ligands is affected by the nature and structure of the alkyl and aryl groups on the terminal positions of the β-diketone moiety. The order of the first dissociation constants (pK^{AH}) among the *Schiff* base ligands studied here are:

$$\mathbf{A1} > \mathbf{A2} > \mathbf{A3} > \mathbf{A4}$$

On the other hand, the second ionization constants (pK^{AH}) has the following order:

$$\mathbf{B2} > \mathbf{B3} > \mathbf{B1} \quad \text{and} \quad \mathbf{A2} > \mathbf{A3} > \mathbf{A1} > \mathbf{A4}$$

Among the **B** and **A** ligands (the expression pK^{AH} for **B** ligands is used for simplicity and denotes the proton coming from the β-diketone tail), the value of pK^{AH} for the fluorinated *Schiff* base (**A4**) is consistently lower than those for acetylacetone derivatives (**A3**, **B3**). The electron withdrawing property of the trifluoromethyl group present in the fluorinated *Schiff* base is responsible for this effect. The relatively high acidity of the *Schiff* bases derived from dibenzoyl-methane could be attributed to the inductive effect of the phenyl rings.

Table 2. Dissociation constants (pK^{AH}) of the ligands in methanol-water at an ionic strength of 0.1 M KNO$_3$

| | pK^{AH} at different temperatures | | | | | | S | r^2 | ΔG_1 | ΔH_1 | ΔS_1 | ΔG_2 | ΔH_2 | ΔS_2 |
| | 288 K | | 298 K | | 308 K | | | | | | | | | |
	pK_1^{AH}	pK_2^{AH}	pK_1^{AH}	pK_2^{AH}	pK_1^{AH}	pK_2^{AH}								
A1	9.42 (0.11)	11.94 (0.03)	9.34 (0.14)	11.78 (0.04)	9.21 (0.21)	11.64 (0.04)	5.59×10^{-7}	0.999	53.31	19.64	−0.11	67.23	24.61	−0.14
A2	9.22 (0.11)	12.24 (0.04)	9.07 (0.09)	12.11 (0.03)	8.93 (0.11)	11.94 (0.03)	3.74×10^{-7}	0.999	51.74	30.69	−0.07	69.09	25.31	−0.15
A3	9.25 (0.14)	12.18 (0.04)	9.08 (0.14)	12.00 (0.04)	8.92 (0.12)	11.81 (0.03)	4.18×10^{-7}	0.999	51.77	26.69	−0.08	68.48	31.47	−0.12
A4	8.96 (0.16)	11.27 (0.04)	8.84 (0.18)	11.12 (0.02)	8.72 (0.22)	10.99 (0.03)	4.36×10^{-7}	0.999	50.44	20.78	−0.10	63.47	23.10	−0.14
B1	–	12.28 (0.03)	–	12.13 (0.05)	–	11.97 (0.04)	4.88×10^{-7}	0.998	–	–	–	69.20	26.16	−0.14
B2	–	12.67 (0.01)	–	12.47 (0.01)	–	12.30 (0.03)	4.28×10^{-8}	0.999	–	–	–	71.17	31.55	−0.13
B3	–	12.62 (0.01)	–	12.44 (0.02)	–	12.05 (0.01)	7.05×10^{-5}	1.000	–	–	–	70.99	48.40	−0.08

B2 and **B3** in 10% (v/v) methanol-water, **A4** in 40% (v/v) methanol-water, **B1**, **A1**, **A2**, and **A3** in 60% (v/v) methanol-water; values in parentheses: standard deviations; S: sum of squares of residuals; r^2: statistical parameter (root of coefficient of determination); ΔG: $T = 298°$K, KJ·mol^{-1}; ΔH: $T_1 = 288°$K, $T_2 = 308°$K, KJ·mol^{-1}; ΔS: $T = 298°$K, J·mol^{-1}·K^{-1}, average values obtained using graphic method and *Gibbs*-Helmholtz equation; ΔS: $T = 298°$K, J·mol^{-1}·K^{-1}

Schiff bases of acetylacetone with aniline and dibenzoylmethane with ethylamine were synthesized for comparison. Their dissociation constants (pK^{AH}) were found to be 12.31 and 11.72 under the same experimental conditions ([L] $= 0.005\,M$, 60% v/v methanol-water, $0.1\,M$ KNO$_3$, $T = 25°$C). Since the synthesized aniline and ethylamine *Schiff* bases contain only one ionizable group (enolic –OH of the β-diketone moiety), it is probable that the pK^{AH} values of the ligands (Table 2) have to be attributed to the dissociation of the enolic –OH of the β-diketone part of these ligands. *Schiff* bases of acetylacetone, benzoylacetone, and thienoyltrifluoroacetone with *o*-phenylenediamine were also synthesized and characterized [26]. The dissociation constants of these ligands (pK^{AH}) are 12.35, 12.12, and 11.83, respectively ([L] $= 0.005$–$0.01\,M$, methanol-water, $0.1\,M$ KNO$_3$, $T = 25°$C). The obtained values for these ligands are in good agreement with pK^{AH} values for **A** and **B** type ligands and confirm the dissociation of the enolic –OH proton of the β-diketone moiety of the ligands. The values of the dissociation constants of ligands **A** are attributed to the dissociation of the –OH proton of the aminophenol moiety of the ligands. The expected values of pK^{AH} of ligands **B** correspond to the dissociation of the ethanolamine moiety of the ligands, they are expected to be more basic since ethanol has a dissociation constant of 15.5 [27].

The dependence of the protolysis constant on the temperature is given in Table 2. The values of ΔH characterize the endothermic dissociation process which is enhanced with temperature. The positive values of ΔH encountered here may be ascribed to the breakage of the covalent bond present in the enolic form of the ligands. The similarity between the ΔH_2 and ΔS_2 values of the dissociation process of the pairs **A1** and **B1** as well as **A2** and **B2** in methanol-water mixtures indicates similar patterns of solvation; **A3** and **B3**, however, have a different pattern.

In addition to the positive values of ΔH, the negative values of ΔS make the dissociation process non-spontaneous and ΔG is positive. The negative ΔS values may be due to the fact that the degree of reorientation and partial immobilization of the methanol and water molecules by H$^+$, the neutral, and the anionic species is greater in water-methanol mixtures than in pure water. From Table 2 one can see that ΔS values are compensated by the ΔH values so that changes in ΔG are smaller than the increments in enthalpy. This sort of compensation has been observed many times for other dissociation reactions and also for other reactions in solutions [28].

The species distribution plot of the *Schiff* base ligands (Fig. 2) shows the neutral species HL (**B** ligands) and H$_2L$ (**A** ligands) at $pH = 1.7$–9. At $pH = 12$–12.3 (**B** ligands) and $pH = 9$–9.5, the ligands are present as a mixture of neutral and ionic species (H$^+L^-$).

On the other hand, at $pH = 11.1$–12 the **A** ligands are present as mixtures of L^- and L^{2-}.

In acidic medium, all *Schiff* bases give cationic species H$_2L^+$ (**B**) and H$_3L^+$ (**A**).

X-ray diffraction

A single crystal of **A3** was prepared using the gel method (methanolic solution of **A3**+*TMS*+H$_2$O). The X-ray diffraction pattern of a single crystal of **A3** was
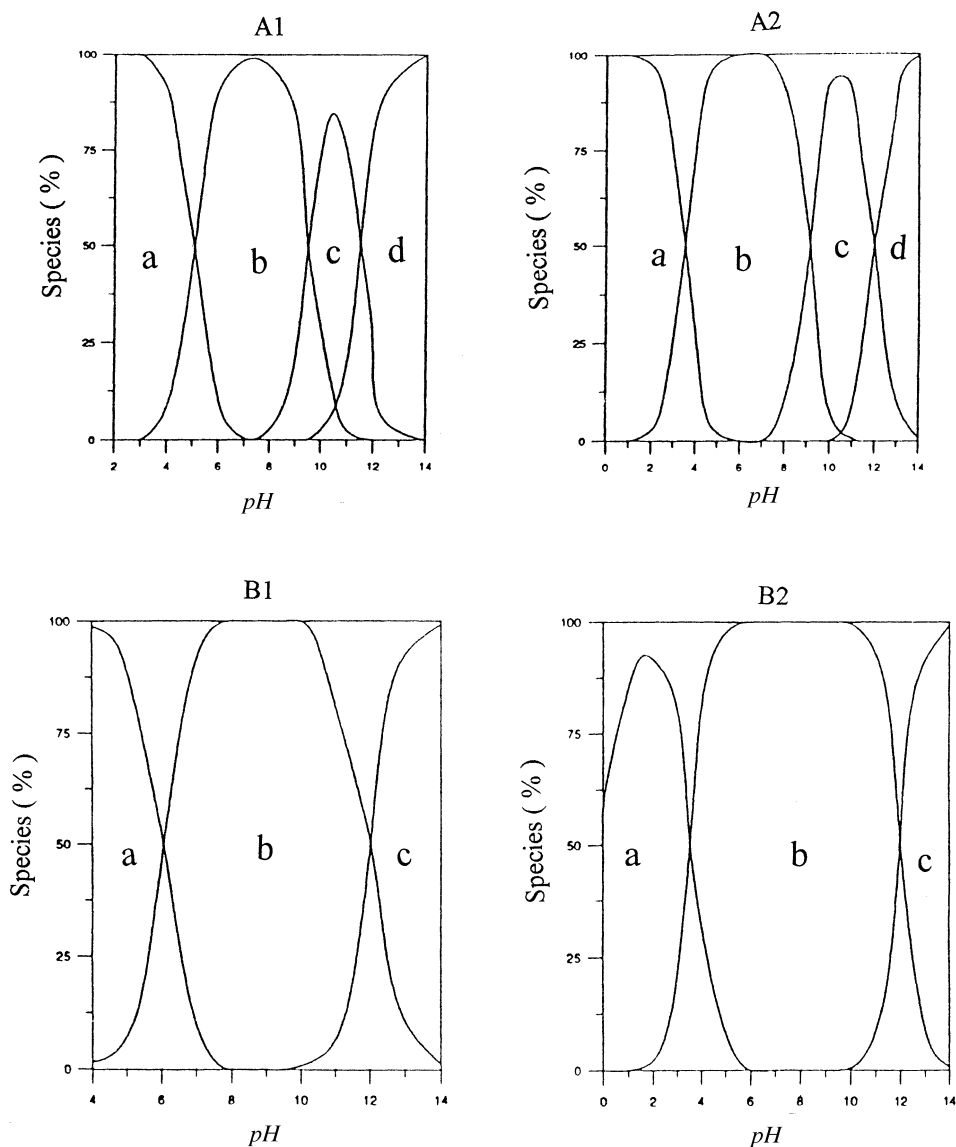
Fig. 2. Distribution curves for different acid-base forms of **A1**, **A2**, **B1**, and **B2** in aqueous methanol at 0.1 M KNO_3 and 25 °C; **A1** and **A2**: a = H_3L^+, b = H_2L, c = HL^-, d = L^{2-}; **B1** and **B2**: a = $H_2L,^+$ b = HL, c = L^-

analyzed using the Multan 80 program [29]. **A3** is orthorhombic; the xy, yz, and zx projections have been obtained and are shown along with the symmetry operations in Fig. 3.

Thermal analysis

The application of TGA to evaluate solid state reactions involving weight loss (or gain) has been studied by a number of workers [30–32]. In the temperature range of 25°C to 160°C, **A1–A4** show colour changes and no weight loss (stability zone).
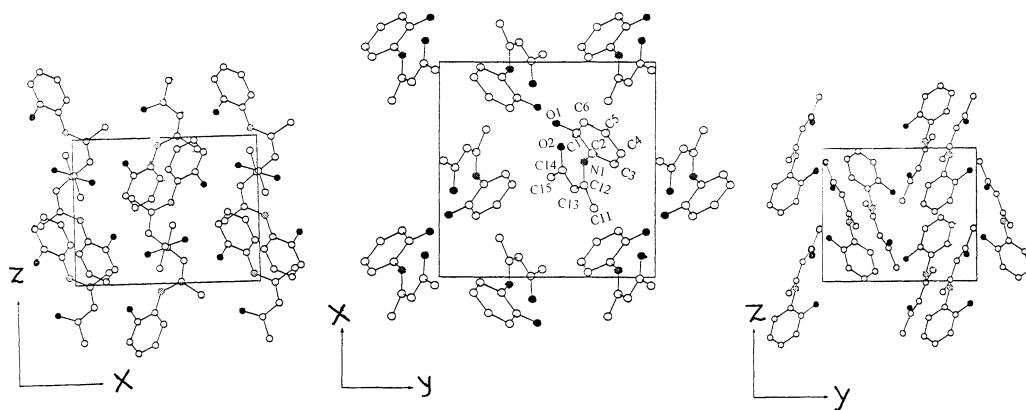
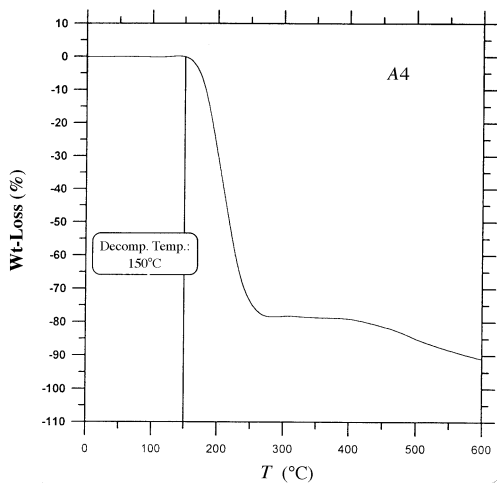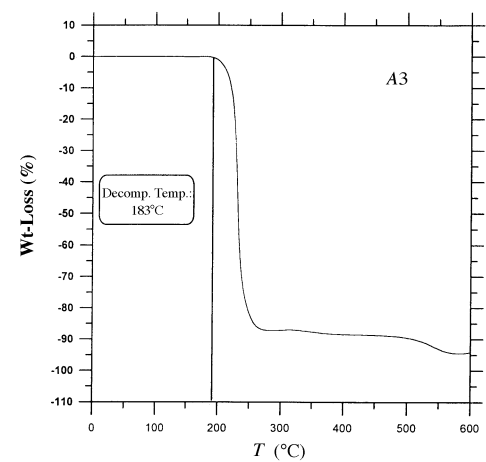**Fig. 3.** XZ, XY, and YZ planes of **A3** single crystal

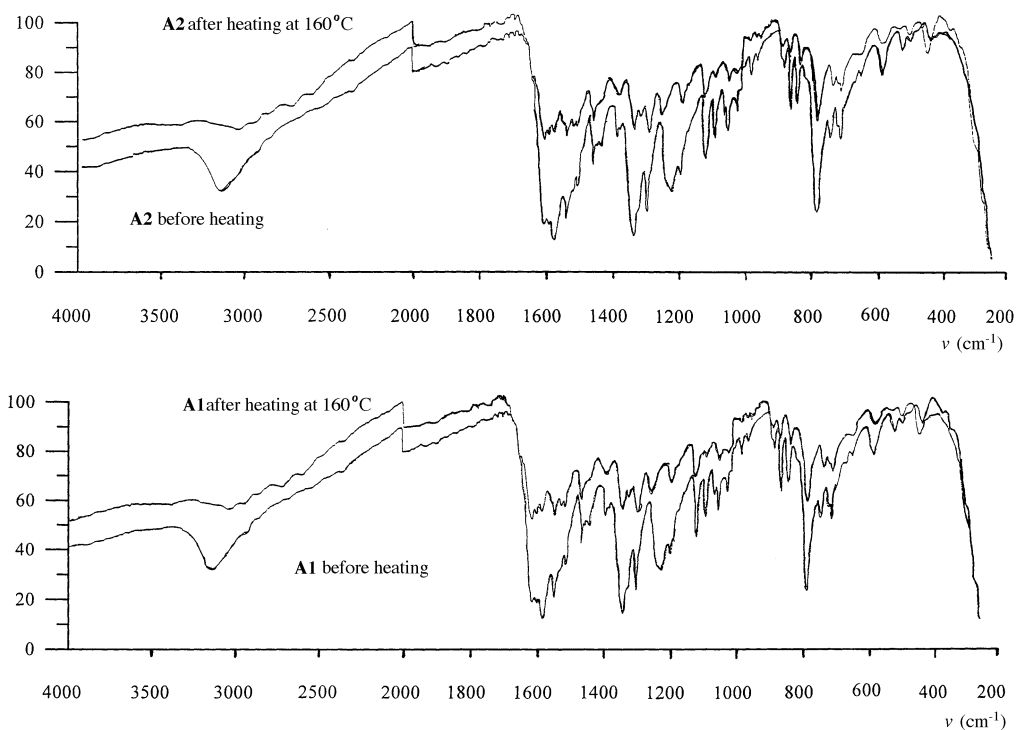**Fig. 4.** Thermogravimetric analysis of **A3** and **A4**

Fig. 5. Effect of heating on the IR band positions of **Al** and **A2**

This may be attributed to the irreversible colour change (thermochromic behaviour) of these ligands as shown in Fig. 4 as an example. Table 1 indicates that each of **A1**, **A2**, and **B1**, **B2** melt at higher temperature than their analogues **A2** and **B3**. These results suggest that the thermal stability of the ligands is greatly influenced by variation in R_1 and R_2. When $R_1 = R_2 =$ phenyl (**A1**, **B1**), the ligands have higher thermal stability, whereas compounds in which $R_1 = R_2 = CH_3$ have lower thermal stability [33]. **A4** shows higher thermal stability which may be attributed to the presence of the five membered thiophene ring [34]. Comparing the two sets of compounds (**A1**, **A2** and **B1**, **B2**), the sharp decrease of the melting point may be attributed to the replacement of aminophenol ethanolamine. The IR spectra of **A1** and **A2** before and after heating at $160°C$ show that the band at $3150 \, cm^{-1}$ which was assigned to stretching vibration of the enolic OH group (ν_{OH}) is still present due to the hydrogen bonding in the resonating structures of the heated samples [35, 36]. Figure 5 indicates that some IR spectra change shape, intensity, and position of some characteristic bands, especially $\nu_{C=C}$ at $1600–1560 \, cm^{-1}$, δ_{C-H} at $1200 \, cm^{-1}$, out-of-plane π_{C-H} deformation at $800 \, cm^{-1}$, and π_{Me-C} at $670 \, cm^{-1}$ [37–39]. The increased degree of crystallinity of **A1** and **A2** after heating (Fig. 6) is ascribed to the electronic donation of the OH group which causes electronic localization as a result of the formation of six chelate rings resulting in an increased band strength. [40] (Scheme 1).
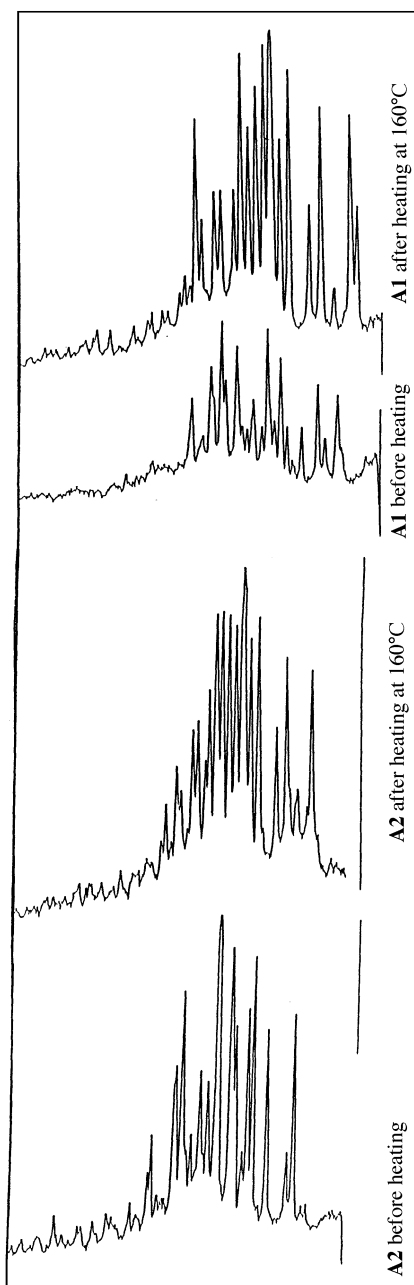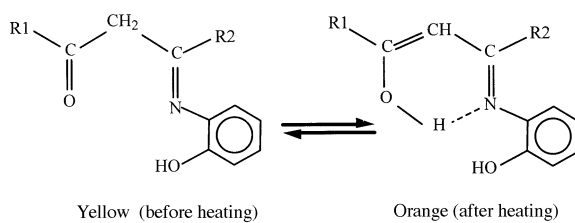
Fig. 6. Effect of heating on the X-ray bands of **A1** and **A2**

Yellow (before heating)   Orange (after heating)

Scheme 1. Keto-enol equilibrium of the ligand

Experimental

Reagents

All chemicals used were of reagent grade; organic solvents were purified by standard methods.

Syntheses

Schiff base ligands were prepared by refluxing a solution of 0.01 mol of the appropriate diketone with 0.01 mol of 2-aminophenol or ethanolamine for 6 hours in the suitable solvent and subsequent recrystallization from ethanol.

Equipment

Elemental analyses were carried out using a Heraeus CHN-Rapid Analyser. Infrared spectra were recorded in the range of 4000 to $200 \, cm^{-1}$ using the KBr disc technique on a Perkin-Elmer 883 spectrophotometer. Single crystal X-ray analysis of **A3** was carried out on a Huber Vierkreis Diffractometer using a MoKα source (7.1069 nm). Photographs of the crystals were obtained using a SZ-PT Olympus microscope fitted with an Olympus camera (Univ. Ulm, Germany). ^{1}H NMR spectra of the ligands were obtained using a 200 MHz Bruker AC200 spectrometer with tetramethylsilane (*TMS*) as internal standard. Thermal analyses of the ligands under investigation were carried out using a STA 409 Netzsch Simultaneous thermoanalyser. All experiments were performed at the University of Ulm, Germany.

A Fisher Accumet *pH*-meter model 825 MP fitted with a Fisher type combined electrode of *pH* range 0–14 was used for *pH* measurements and calibrated according to *Irving* [15]. All titrations were performed in a double-jacket thermostatted cell. *pH* readings recorded in methanol-water at an ionic strength of $0.01 \, M$ KNO$_3$ were converted to hydrogen ion activity [16]. The MINSQ non-linear least-square computer program [17] was used to calculate acidity constants and species distribution diagrams (performed on an IBM personal system model 55SX).

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