

STUDIES ON THE THERMAL BEHAVIOUR OF MONO- AND DI-IMINES OF SOME DIAMINONAPHTHALENES

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The mono- and di-imines of some diaminonaphthalenes were prepared using a solid solid reaction technique. Their structures were studied using elemental analysis, infrared and electronic spectra. The thermal behaviour of the obtained compounds and their solid solid preparation reactions have also been studied. The energies of activation as well as the reaction orders of those reactions were determined.

A much work was done on the metal complexes involving symmetrical Schiff bases. Recently, attention has been paid to complexes involving non-symmetrical Schiff bases due to their importance in varying the properties of the complexes. Furthermore the reactivity and redox potential of the central metal in those complexes are very sensitive to the nature of the chelate ring. But the problem is, the difficult preparation of such non-symmetrical bases due to instability of mono-imines which in turn gives the non-symmetrical diimines, thereat the known non-symmetrical diimines have been obtained by a template synthesis and have not been isolated in free (non-coordinated) state [1-4] except those have been obtained recently by the method of Costes *et al.* [5]. Due to our interest in the solid state reactions we reported recently a successful, simple and economic method for preparation of non-symmetrical diimines using solid state reactions [6]. In the present work the reproducibility of the method was checked to other Schiff bases, especially the preparation of the unstable (in solution) mono-imines which are the important stage of such reactions. Also the thermal behaviour of the obtained compounds as well as the kinetic parameters of those solid reactions were discussed.

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Experimental

Preparation of Schiff bases

The Schiff bases I, II, III and IV were prepared using a solid-solid reaction technique as follows:

Ligands I and II were prepared by mixing the molar ratios (1:1) and (1:2) of 1,5-diaminonaphthalene and 2-hydroxy-1-naphthaldehyde respectively. The reaction mixtures were heated up to 90° in drying oven for 30 minutes. Red compounds were obtained.

Ligands III and IV were prepared by mixing the molar ratios (1:1) and (1:2) of 2,3-diaminonaphthalene and 2-hydroxy-1-naphthaldehyde respectively. The reaction mixtures were heated up to 90° for 30 minutes. A red and a dark yellow compounds were obtained.

The elemental analysis was carried out in N. R. C. Dokki-Cairo-Egypt. IR spectra were carried out in KBr discs using a Perkin-Elmer 598 (4000-200 cm^{-1}) spectrophotometer. Electronic spectra were recorded in CHCl_3 using a Unicam SP-8000 spectrophotometer. Thermal analysis was measured using a Shimadzu XD-30 thermal analyzer. X-ray powder diffraction was recorded using a Shimadzu XD-3 diffractometer by applying $\text{CuK}\alpha$ line.

Results and discussion

The IR spectra of ligands I, II, III and IV were depicted in Fig. 1. The spectra display characteristic bands near 1080 cm^{-1} , 1580 cm^{-1} and 1610 cm^{-1}

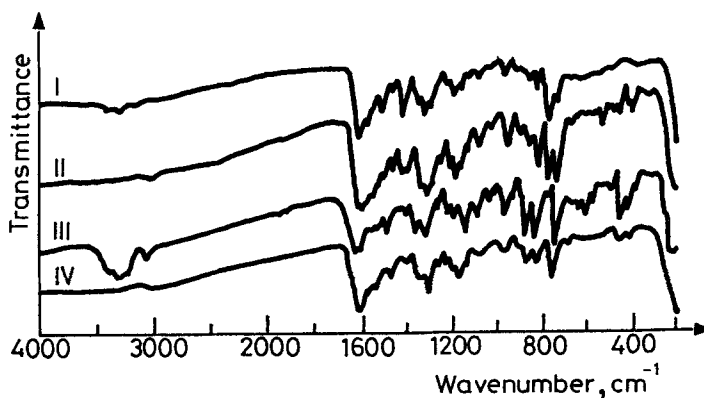


Fig. 1 IR Spectra of compounds I, II, III and IV

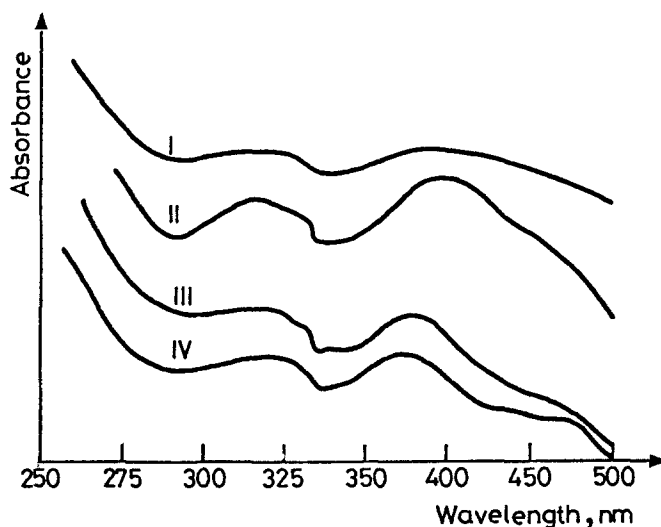


Fig. 2 Electronic spectra of compounds I, II, III and IV

were assigned to $\nu\text{C-OH}$, aromatic ring stretching and $\nu\text{C}=\text{N}$ respectively. The spectra of II and IV display also a very broad band with lower intensity near $3400\text{-}3200\text{ cm}^{-1}$ and another band at 1620 cm^{-1} were assigned to νOH (hydrogen bonded) and δOH respectively. Whilst the spectra of I and III show additional bands near $3400\text{-}3200\text{ cm}^{-1}$ and 1620 cm^{-1} were assigned to νNH_2 (three bands) and δNH_2 respectively. The appearance of νNH_2 band in the spectra of I and III and its disappearance from those of II and IV confirming the formation of the "half unit" Schiff bases, I and III (mono-imine).

Electronic spectra

The electronic spectra of the compounds show three bands (Fig. 2) around 320 nm, 380-400 nm and 450-470 nm. The first band was assigned to $n - \pi^*$ [7] and the other two bands were assigned to charge transfer (C. T.) [8, 9]. The appearance of new bands at 380-400 nm and 450-470 nm (C. T.) in the spectra of the compounds on comparison with those of the reactants emphasize the formation of the compounds. Elemental analysis (Table 1), infrared and electronic spectral data suggest the following structures of the compounds.

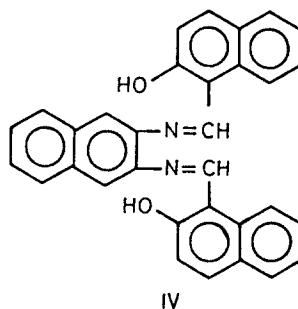
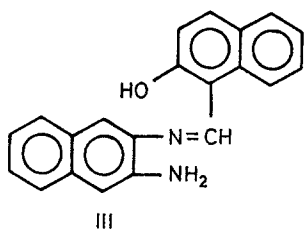
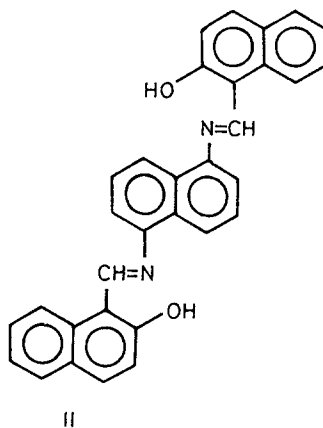
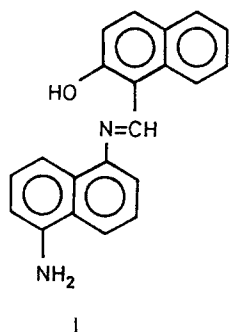


Table 1 Elemental analysis

Compound	C, %	H, %
I	80.57(80.77)	5.35(5.13)
II	82.52(82.40)	6.53(6.40)
III	80.20(80.77)	5.28(5.13)
IV	82.34(82.40)	6.31(6.40)

Cal. Analysis in parentheses

Thermal studies

The thermal solid state reactions for preparation of ligands I, II, III and IV were studied using thermal differential analyzer (DTA). Figure 3 shows the DTA curves of the prepared ligands I, II, III and IV and their reactants mixtures I_a, II_a, III_a and IV_a.

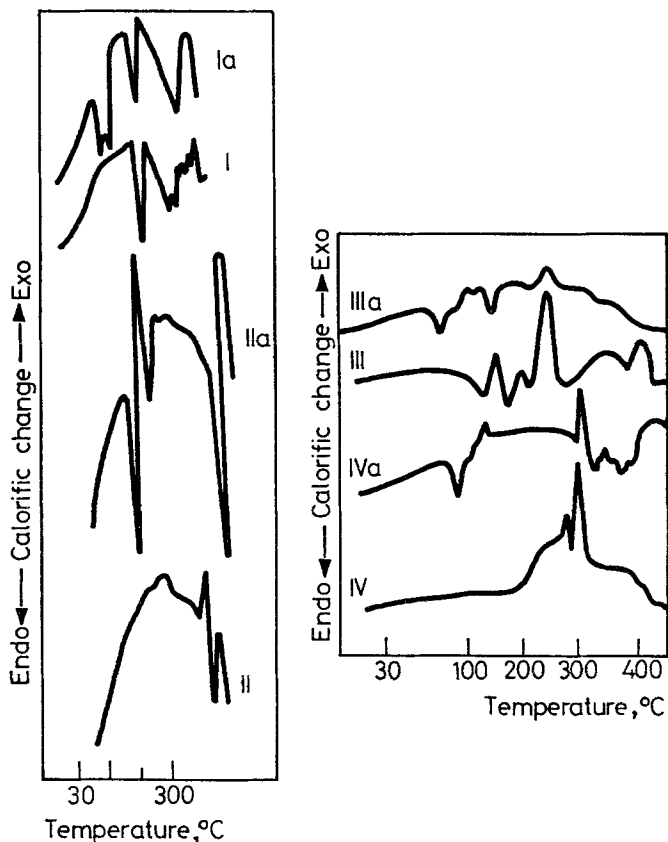


Fig. 3 DTA curves of the compounds and their solid state reactions

The curve of I_2 (Fig. 3) shows a splitted endothermic peak around 85° followed by sharp and broad endothermic peaks at 170° and 300° respectively. These peaks were assigned to melting of 2-hydroxy-1-naphthaldehyde (m.p. $82-85^\circ$) through the formation of compound, (I). This assignment was confirmed by the disappearance of that peak in the DTA curve of the previously prepared compound, (I). Again the peaks at 170° and 300° were assigned to phase transition and material decomposition. The phase transition peak at 170° was also confirmed by X-ray powder diffraction and IR measurements. The IR spectra of (I) and its heated sample up to 170° are mainly the same except some minor changes in the shape as well as the arbitrary intensity and sometimes the frequency of some peaks (Fig. 4a). This might be

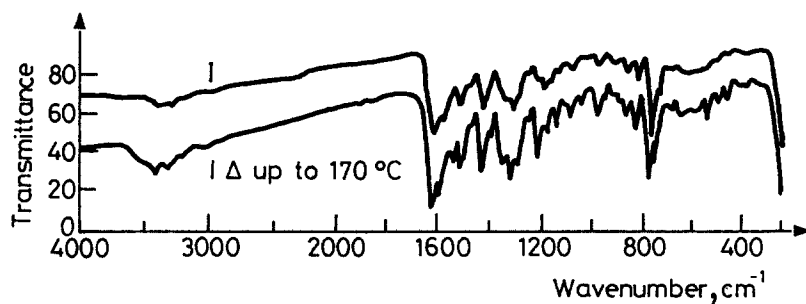


Fig. 4a IR spectra of I and its heated sample

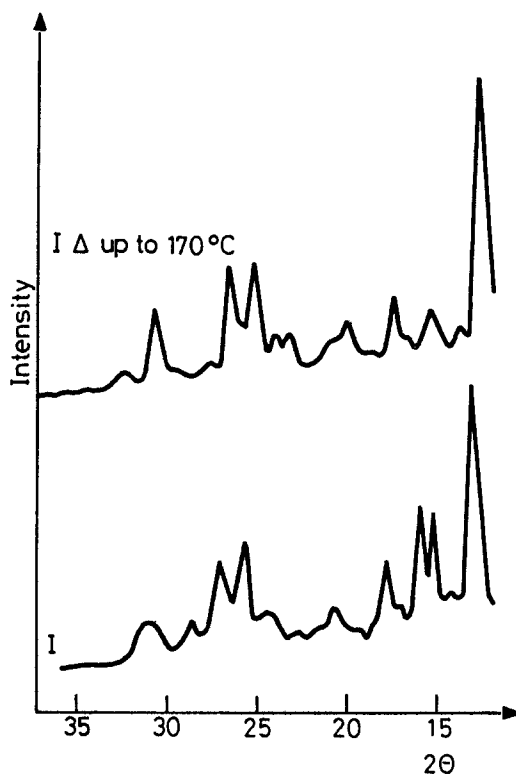
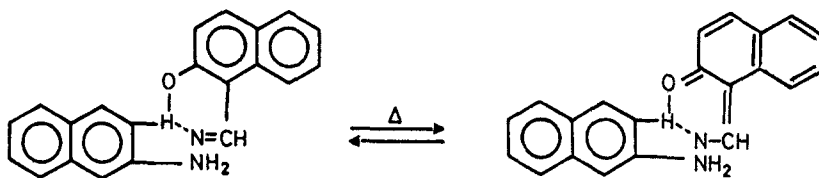


Fig. 4b X-ray power diffraction of I and its heated sample

due to the crystal packing changes as a result of phase change [6, 10-12]. This phase change was also confirmed by the different X-ray diffraction patterns of (I) and its heated sample up to 170° (Fig. 4b).

The thermal curve of II_a (Fig. 3) shows a sharp endothermic peak at 77° was assigned to the melting of 2-hydroxy-1-naphthaldehyde (m.p. 82-85°) followed by a sharp exothermic peak at 90° was assigned to the formation of the compound (temperature of preparation 90°). These assignments were confirmed by the disappearance of those peaks in the DTA curve of the previously prepared (II). The thermal curve shows also a sharp endothermic peak at 350° was assigned to material decomposition. It is clear that (II) shows higher thermal stability than (I).

The DTA curve of (III_a) (Fig. 3) shows an endothermic peak at 77° was assigned to the formation of the compound through the melting of 2-hydroxy-1-naphthaldehyde. This assignment was confirmed by the absence of that peak from the DTA curve of (III). The thermogram shows also a number of endothermic peaks at 155°, 180° and 220° were assigned to phase transition (the colour changes from red to brown), another phase transition (the colour changes from brown to green) and the melting of the compound (m.p. 220). The phase transition peaks assignments were confirmed by X-ray powder diffraction and IR measurements. The IR spectra of (III) and its heated samples up to 155° and 180° are mainly the same except some minor changes in the shape as well as arbitrary intensity and sometimes the frequency of the peaks (Fig. 5a). This might be attributed to the crystal packing changes as a result of the phase changes [6, 10-12]. X-ray diffraction shows different patterns for (III) and its heated samples up to 155° and 180°, indicating the presence of those phases (Fig. 5b). The obtained colour changes against heat treatment of the compound may be attributed to the Keto-enol tautomerism, predicting thermochromic properties of that compound as numerous Schiff bases [13].



Finally the thermal curve shows a number of exothermic peaks at 240°, 330° and 390° were assigned to material decompositions.

The thermal curve of (IV_a) (Fig. 3) shows an endothermic peak at 77° was assigned to the formation of the compound through the melting of

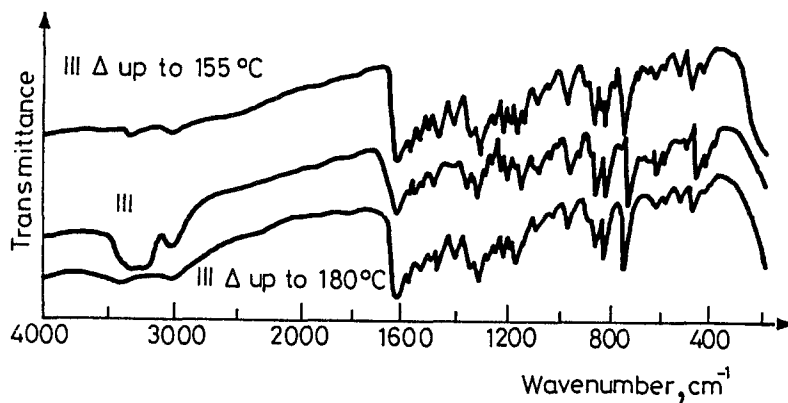


Fig. 5a IR spectra of III and its heated samples

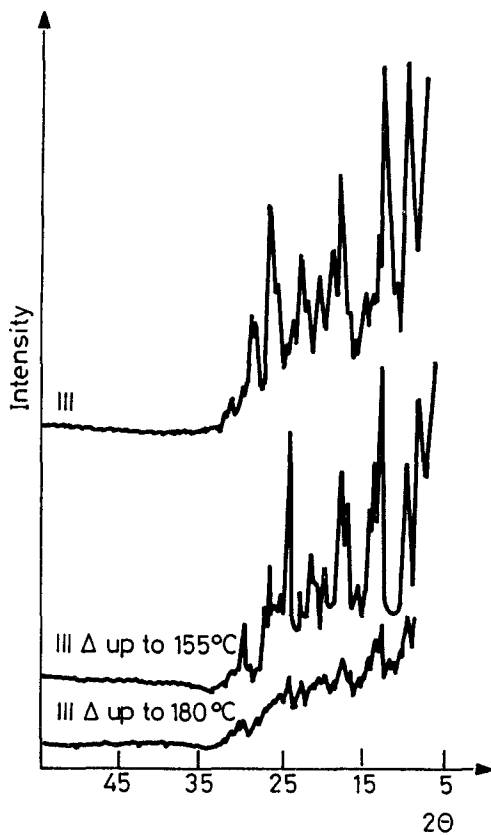


Fig. 5b X-ray powder diffraction of III and its heated samples

2-hydroxy-1-naphthaldehyde. This peak disappeared in the DTA curve of (IV) confirming the above assignment. The thermogram shows also an endothermic peak at 250° and an exothermic peak at 260° were assigned to the melting of the compound (m.p. 250) and material decomposition respectively. It is shown that compound (IV) shows higher thermal stability than (III).

From the above argument, it is concluded that:

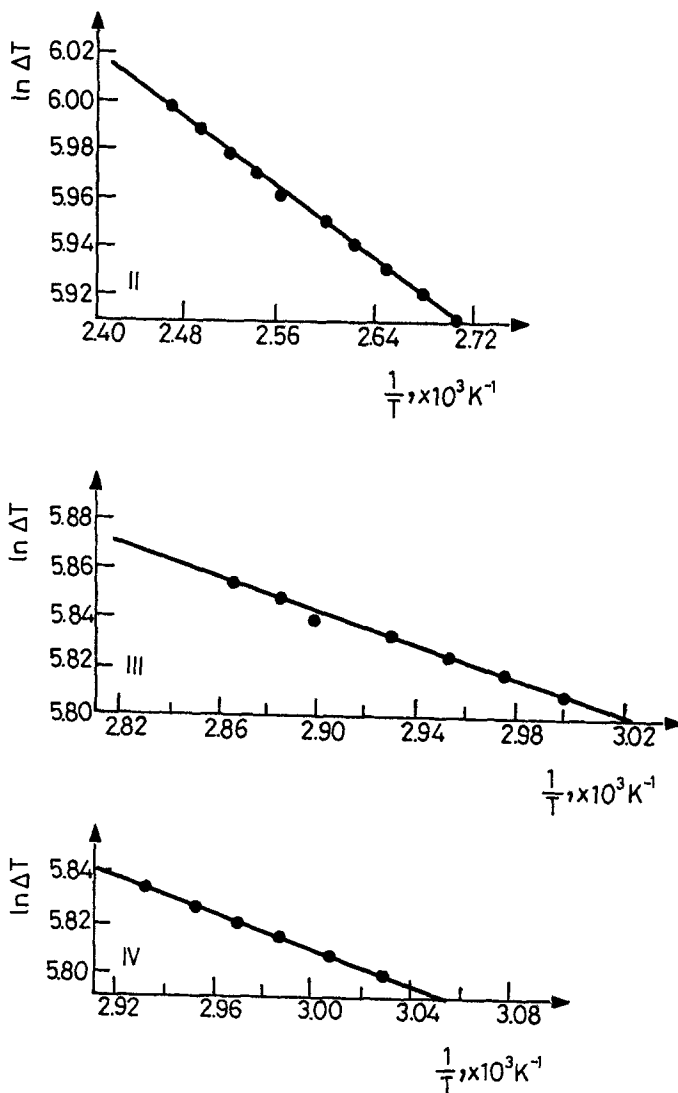


Fig. 6 Plots constructed from DTA curve

(i) Compounds (I) and (II) are thermally stable than (III) and (IV), this may be due to steric effects in (III) and (IV).

(ii) The mono-imines (I) and (III) show lower thermal stability than di-imines (II) and (IV), in good agreement with the previous work [5].

The energies of activation (E_a) of the solid-solid formation reactions were determined from the DTA curves using the method of Piloyan *et al.* [14]. E_a was determined from the slope of lines (Fig. 6). The reactions are nearly first order as indicated in Table 2. The orders were estimated by the peak asymmetry method [15].

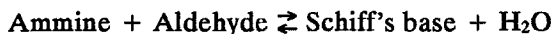
Table 2 The values of reaction orders and activation energies (E_a)

Compound	E_a , kJ · mole ⁻¹	Order
II	2.8	0.95
III	2.7	0.97
IV	2.8	0.97

It is noteworthy that the obtained compounds were also prepared without any heat dealing. But the formation reaction takes a long time for completion. This leads to the following considerations:

(i) The melting of 2-OH-1-naphthaldehyde is not necessary for the reaction completion.

(ii) The heat assists the water loss from the reaction, leading a catalytic effect.



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Zusammenfassung — In einer Feststoffreaktion wurden Mono- und Diimine einiger Diaminonaphthalene hergestellt. Die Struktur der Produkte wurde mittels Elementaranalyse, IR- und Elektronenspektren untersucht. Weiterhin wurde das thermische Verhalten der erhaltenen Verbindungen sowie die Feststoffreaktionen zu ihrer Herstellung näher untersucht, wobei Aktivierungsenergien und Reaktionsordnungen ermittelt wurden.