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THERMAL SYNTHESIS OF NOVEL 'HALF UNIT' SCHIFF BASES

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ABSTRACT

The 1 : 1 molar ratio solid state thermal reactions of 2,6-diaminopyridine, carbohydrazide and 2,6-diamino-4-chloropyrimidine with each of 2-hydroxy-1-naphthaldehyde, 2,4-dihydroxybenzaldehyde and 2,6-diacetylpyridine produced (1 + 1) condensation products ('half units'). These solid state reactions have been studied using differential thermal analysis (DTA). The products of the reactions were identified using elemental analysis and IR spectroscopy. The activation energies and orders of the reactions were determined from the DTA calorigrams.

INTRODUCTION

There are numerous accounts in the literature describing the chemistry of Schiff bases. Schiff bases result from the condensation of two molecules of a keto compound with one molecule of diamine, even where equimolar amounts of the reactants are used. A few of the Schiff bases reported so far arose from the condensation of the carbonyl function with only one end of the diamine. These are referred to as 'half unit' Schiff bases. They have been prepared by template synthesis and isolated as their metal complexes or by partial hydrolysis of symmetrical Schiff bases [1–4]. In a very few cases, free 'half unit' Schiff bases have been prepared [5–8]. All the above preparations were performed in solution.

The present article reports a solid state thermal method for the synthesis of 'half unit' Schiff bases.

EXPERIMENTAL

Materials

Reagent grade chemicals were used. Thermal treatments were carried out using a Shimadzu XD-30 thermal analyser. IR spectra were measured in KBr discs using a Perkin–Elmer 598 (4000–200 cm^{-1}) spectrophotometer.

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TABLE 1

Maximum peak temperatures, activation energies and orders of reactions and melting points of products

Compound	T_m (K)	E_a (kcal^{-1} mol^{-1})	n	Effect of heat (° C)
$\mathbf{I}_a$	355	24.32	1	165 [a]
$\mathbf{I}_b$	355	38.46	1	185 [a]
II	365	15.96	1	115 (changed to red)
III	358.5	34.51	1	150 [a]
IV	381.4	19.87	1	167 [a]
V	355	20.62	1	159 [a]
VI	358	15.52	1	230 [a]
VII	346			70 (melting)

[a] Decomposition.

Carbon, hydrogen and nitrogen were determined at the analytical unit of the University of Cairo.

Preparation of 'half unit' Schiff bases

The 'half unit' Schiff bases were prepared by heating a finely divided mixture of equimolar amounts of diamine and carbonyl compounds in an electric furnace for about 30 minutes at the temperatures listed in Table 1. The products were recrystallized from ethanol, except for those resulting from the reactions of 2-hydroxy-1-naphthaldehyde with 2,6-diaminopyridine and with carbohydrazide, for which crystallization led to the formation of (1 + 2) condensation products.

RESULTS AND DISCUSSION

The 1 : 1 molar ratio solid state thermal reactions of 2,6-diaminopyridine and of carbohydrazide with 2-hydroxy-1-naphthaldehyde and with 2,4-dihydroxybenzaldehyde led to the formation of 'half unit' Schiff bases **I**–**IV** respectively. The 1 : 1 molar ratio reactions of 2,6-diacetylpyridine with 2,6-diamino-4-chloropyrimidine, with carbohydrazide and with 2,6-diaminopyridine produced 'half unit' Schiff bases **V**–**VII** respectively. The 1 : 1 molar ratio reaction of $\mathbf{I}_a$ with 2-hydroxy-1-naphthaldehyde produced the (1 + 2) condensation product $\mathbf{I}_b$.

The thermoproducts obtained by heating a powdered mixture of equimolar amounts of the reactants at the maximum temperature of the endothermic peak (T_m) (Fig. 1 and Table 1) were investigated by means of elemental analysis and IR spectra.

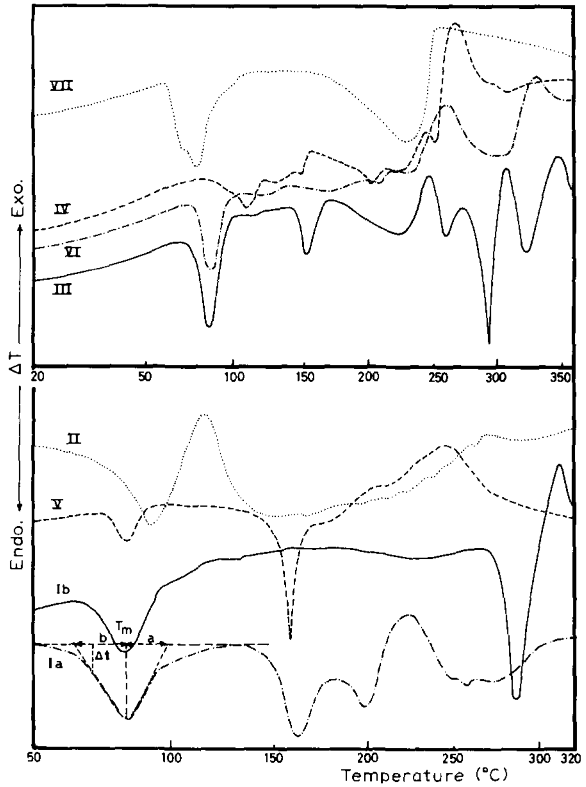


Fig. 1. DTA calorigrams of the solid state thermal reactions leading to the formation of compounds **I–VII**.

The analytical and IR spectral results (Tables 2 and 3, respectively) are consistent with the chemical formulations in Fig. 2.

The IR spectral data indicate that compounds **I**$_a$, **I**$_b$ and **III** have intramolecular hydrogen bonding (O–H · · · N), shown by absorption near

TABLE 2

Half unit Schiff bases: analytical data and colours

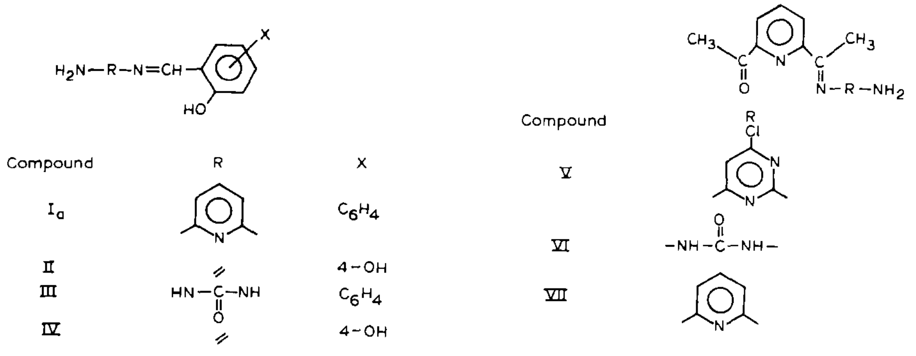
Compound		C [a](%)	H [a](%)	N [a](%)	Colour
I$_a$	($C_{16}H_{13}N_3O$)	72.3 (73.0)	4.9 (4.9)	15.8 (16.0)	orange
I$_b$	($C_{27}H_{19}N_3O_2$)	77.3 (77.7)	4.5 (4.6)	9.8 (10.1)	red
II	($C_{12}H_{11}N_3O_2$)	62.4 (62.9)	4.6 (4.8)	18.6 (18.3)	reddish brown
III	($C_{12}H_{12}N_4O_2$)	59.3 (59.0)	4.7 (4.9)	22.8 (23.0)	pale yellow
IV	($C_8H_{10}N_4O_3$)	45.3 (45.7)	4.7 (4.8)	26.6 (26.7)	pale yellow
V	($C_{13}H_{12}N_5OCl$)	53.7 (53.9)	41. (4.2)	24.4 (24.2)	white
VI	($C_{10}H_{13}N_5O_2$)	51.7 (51.1)	5.7 (5.5)	29.5 (29.8)	yellow
VII	($C_{14}H_{14}N_4O$)	66.4 (66.1)	5.3 (5.5)	22.3 (22.0)	yellow

[a] Calculated values in parentheses.

TABLE 3

Infrared spectra [a]

Band assignment	Compound							
	I_a	I_b	II	III	IV	V	VI	VII
νO–H	3480(w)	3440(br)	3450(w), 3100(w, br)	3420(sh)	3440(br), 3120(w, br)			
νNH_2	3448(m) 3400(w), 3318(m), 3200(w)		3360(br), 3200(w)	3360(m), 3330(w), 3300(s)	3360(s), 3340(sh), 3250(w)	3480(s), 3365(s), 3315(sh), 3230(w), 3180(s)	3405(m), 3350(m)	3440(s), 3380(s), 3330(s), 3190(s)
νNH				3200(s)	3200(w)		3190(m)	
νC–H (azomethyne)	3025(w)	3050(w)	3040(w)	3080(w)	3040(w)			
νC=O				1690(s)	1665(s)	1680(s)	1690(s), 1655(s)	1700(s)
δNH_2	1625(s)		1620(s, br)	1655(sh)	1633(s)	1645(sh)	1645(sh)	1640(sh)
νC=N	1615(sh)	1628(s)	1610(sh)	1620(s)	1615(sh)	1630(s)	1635(sh)	1630(s)
δOH	1210(s)	1210(s)	1220(m)	1210(s)	1225(s)			
νC–OH	1070(m)	1085(m)	1075(m)	1080(m)	1130(s)			
α,β-substituted naphthyl ring	834(s)	834(s), 738(s)		840(s), 748(s)				
benzene ring (out of plane)			730(s)		745(s)			
pyridine ring breathing mode	1015(m)	1015(s)	1020(w)			1020(s)	1020(m)	1018(s)
substituted pyrimidine ring (deformation bands)						620(w), 595(s), 480(sh)		



Chemical formulations of compounds (I_a - IV)

Chemical formulations of compounds (V - VII)

Fig. 2. Suggested chemical formulations of the 'half unit' Schiff bases.

3440 cm^{-1} [9]. Compounds **II** and **IV** show two absorption bands near 3120 cm^{-1} and 3450 cm^{-1}, attributable to intramolecular hydrogen bonding ($O-H\cdots N$) [10] and free νOH, respectively. The IR spectra of all the compounds show absorption bands within the range 3448–3200 cm^{-1}, attributable to νNH_2. The spectra of compounds **III**, **IV** and **VI** display a band near 3200 cm^{-1}, attributable to νNH. The spectra of compounds **I–IV** show a weak band near 3050 cm^{-1}, attributable to $\nu C-H$ of the azomethine group. The spectra of compounds **III–VII** shows a strong band at 1665–1700 cm^{-1}, attributable to $\nu C{=}O$. The spectra of all the compounds display a strong shoulder band near the region 1635–1610 cm^{-1}, attributable to $\nu C{=}N$. δNH_2, δOH and $\nu C-OH$ bands appear near the regions 1655–1620 cm^{-1}, 1225–1210 cm^{-1} and 1130–1070 cm^{-1} respectively. The spectra of compounds $\mathbf{I_a}$, $\mathbf{I_b}$ and **III** show two strong bands near 840–834 and 748–738 cm^{-1}, attributable to α- and β-substituted naphthyl rings, whilst compounds **II** and **IV** show a strong band near 745 cm^{-1}, attributable to vibration of C–H out of the plane of the phenyl ring. The spectra of all the compounds except **III** and **IV** show a band near the region 1020–1015 cm^{-1}, attributable to the breathing mode of the pyridine ring. The spectrum of compound **V** shows three bands at 620, 595 and 480 cm^{-1}, attributable to deformation bands of the pyrimidine ring.

The formation of the 'half unit' Schiff bases is explained as follows

$$H_2N-R-NH_2(s) + R_1R_2C{=}O(s) \xrightarrow{heat} R_1R_2C{=}N-R-NH_2 + H_2O \qquad (1)$$

Solid state thermal reactions of 'half unit' Schiff bases with the same or with a different carbonyl compound to produce (1 + 2) condensation Schiff base products (symmetrical or unsymmetrical) did not succeed, except for compound $\mathbf{I_a}$ which reacted with 2-hydroxy-1-naphthaldehyde and produced $\mathbf{I_b}$. However, if these reactions are carried out in ethanolic solution, symmetrical or unsymmetrical Schiff bases are produced. The formation of unsymmetrical Schiff bases is explained as follows

$$\mathrm{R_1R_2C{=}N{-}R{-}NH_2 + O{=}CR_3R_4} \xrightarrow[\mathrm{C_2H_5OH\ (1:1)}]{\text{heat}} \mathrm{R_1R_2C{=}N{-}R{-}N{=}CR_3R_4 + H_2O} \tag{2}$$

Reaction (2) represents a new route for the synthesis of unsymmetrical Schiff bases, which will be the subject of a separate report [11].

To ensure that these reactions are solid state reactions, all of them were repeated using a melting point measurement apparatus provided with a microscope. It was found that all the reactions were not accompanied by melting of both or one of the reactants except the reaction that lead to the formation of compound **VII**. This reaction therefore can not be studied kinetically.

The orders and energies of activation (E_a) of the condensation reactions were determined from DTA calorigrams (Fig. 1). The orders of the reactions were evaluated using Reich's empirical relation [12]

$$n = 1.26\, S^{1/2} \text{ and } S = \frac{a}{b}$$

where n is the reaction order and S is the peak shape factor. The values of a and b were calculated as shown in Fig. 1. The calculated values of n (Table 1) indicate that all the reactions are first order.

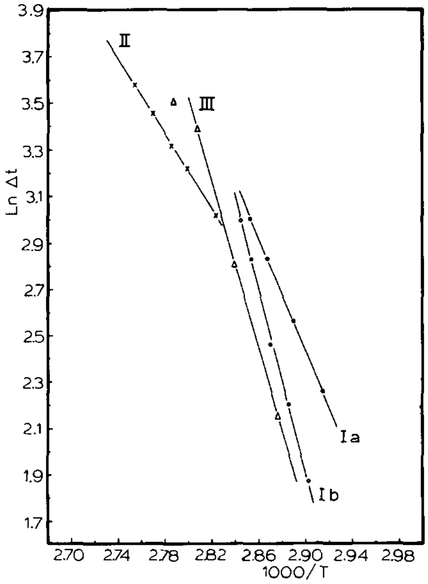


Fig. 3. Plot of ln Δt vs. $1000/T$ ($\mathrm{K^{-1}}$) for compounds **I**–**III**.

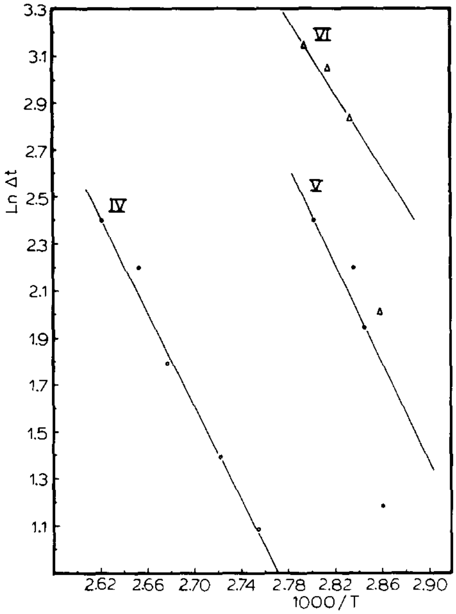


Fig. 4. Plot of ln Δt vs. $1000/T$ (K^{-1}) for compounds **IV–VI**.

The energies of activation listed in Table 1 were calculated using the formula of Piloyan et al. [13]

$$\ln \Delta t = C^1 - \frac{E_a}{RT}$$

where Δt is the deviation from baseline (its values being taken directly from the DTA curve in units of length (cm or mm), as shown in Fig. 1), C^1 is a constant, E_a is the energy of activation, R is the universal gas constant (equal to 1.987 cal K^{-1} mol^{-1}) and T is the absolute temperature. The plot of ln Δt versus $1000/T$ gave a straight line (Figs. 3 and 4), with a slope of $-E_a/R$.

REFERENCES

1 R.O. Elder, Aust. J. Chem., 31 (1978) 35.
2 H.A. Goodwin and F. Lions, J. Am. Chem. Soc., 82 (1960) 5013.
3 W.N. Wallis and S.C. Cummings, Inorg. Chem., 13 (1974) 991.
4 A.C. Braithwaite, C.E.F. Rickard and T.N. Waters, J. Chem. Soc., Dalton Trans., (1975) 2149.
5 A.P. Summerton, A.A. Diamantis and M.R. Snow, Inorg. Chim. Acta, 27 (1978) 123.
6 P.G. Beckingsale, A.T. Morcom, C.E.F. Rickard and T.N. Waters, J. Chem. Soc., Dalton Trans., (1977) 2135.
7 J.P. Costes and G. Cros, C. R. Acad. Sci., 294-II (1982) 173.

8 H. Adams, N.A. Bailey, J.P. Costes, D.E. Fenton and J.R. Tate, International Conference on Inorganic Stereochemistry, Reading, England, 1982, Poster A-25.
9 K. Morishige, J. Inorg. Nucl. Chem., 40 (1978) 843.
10 R.C. Aggarwal, Rashmi Bala and R.L. Prasad, Spectrochim. Acta, 24 A (6) (1986) 1329.
11 F.A. El-Saied, to be published.
12 T. Reich, J. Inorg. Nucl. Chem., 28 (1966) 1329.
13 G.O. Piloyan, I.D. Ryabchikov and O.S. Novikova, Nature, 5067 (1966) 1229.