Thermal Fragmentation of 1,2-Dicyanoethylenediamine-N-butadiene and Four of (*p*-substituted benzylidenes)-1,2-dicyanoethylenediamine

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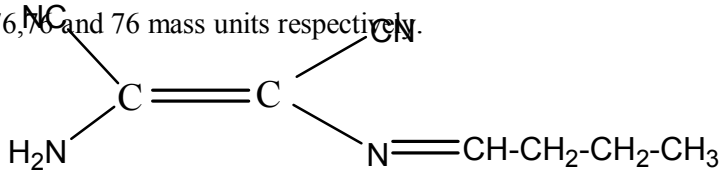
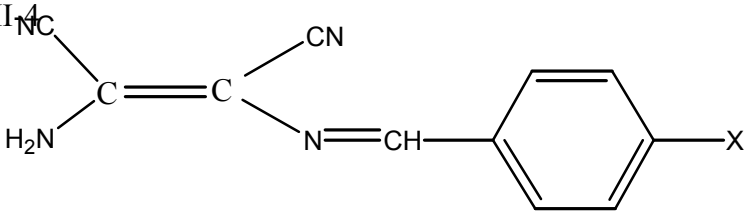
Abstract

The thermal decomposition of 1,2-Dicyanoethylenediamine-N-butadiene (HI-4) ; 1,2-Dicyanoethylenediamine-N-benzylidene (HI-3) and three of *p*-substituted benzylidene, (HI-1) *p*-methoxy , (HI-2) *p*-N,N$^{/}$-dimethylamine and (HI-5) *p*-nitro have been investigated.All compounds HI-(1,2,3,4,5) have been followed through the same fragmentation mechanism.Compounds HI-1 ; HI-3 ;HI-4 and HI-5 were degradated at carbon-nitrogen bond but HI-2 compound was degradated at phenyl-CH bond . these compounds HI-(1,2,3,4,5) lost initially 76,121,76,76 and 76 mass units respectively.



Comp. HI-4



X=OCH_3 comp. HI-1 ; X=$N(CH_3)_2$ comp. HI-2 ;
X=H comp. HI-3 ; X=NO_2 comp. HI-5

Scheme 1

الخلاصة

فحص التجزؤ الحراري لـ2،1-ثنائي سيانواثيلين-N-بيوتادين(HI-4) ولـ(2،1-ثنائي سيانواثيلين ثنائي أمين- N- بنزيليدين (HI-3) ولثلاثة من البنزيليدنيات المعوضة في موقع بارا, (HI-1) بارا-ميثوكسي و (HI-2) بارا-N,N/-ثنائي مثيل أمين و(HI-5) بارا-نايترو وإتضح أن جميع المركبات تخضع لميكانيكية تجزؤ متقاربة حيث وجد إن المركبات HI-1 ، HI-3، HI-4، HI-5تتكسران من خلال الأواصر(كاربون-نتروجين) لكن المركب HI-2 يتكسر من خلال الأصرة فنيل-CH ووجد إن المركبات HI-(1,2,3,4,5) تلفظ إبتدائياً 76 ،121 ,76 ،76،76 وحدة كتلة على التوالي .

Introduction

Many benzylidene anilines have prepared previously.The earlier studies have included mainly analysis of various spectral data [1,2],Kinetics of hydrolysis [3,4] and complexation with transition metal ions[5] ,Iodine [6] and benzoquinones [7,8,9].Avery limited work has been done previously on the thermal decomposition of some substituted Bis(benzylidenes)-1,3-diamino-2-propanol has been reported [10,11].In this work the thermal decomposition of butalidene and a series of various benzylidenes aliphatic diamines derived from aliphatic , aromatic aldehydes and 1,2-Dicyanoethylenediamine [12] has been studied and discussed.

Experiment

Details of the elemental analysis,UV,mass spectra were discussed elsewhere [13,14].All compounds HI-(1,2,3,4,5) Scheme 1 used throughout this work are well known compounds and were prepared by condensation of 1:1 (w/w) of 1,2-Dicyanoethylenediamine and butalidenes or the corresponding benzylidehyde.They were purified and characterized according to the well established procedures described in literature [1,2,3,4,5,8,12.13] unless indicated otherwise.The physical properties,the thermogravimetric analysis and IR spectra data of these compounds are sumarised in Table 1and Table 2 respectivily .The infrared spectra were measured on Pye-Unicam Sp 3-300 spectrophotometer as KBr discs.The thermogravimetric TG and DTG analysis were carried out

using Seiko instruments TG and DTG thermoanalyser which can be standarize with platinium metal and using nitrogen gas to speed of 50 ml/min and a heating rate of 20 ^{0}C/min .

Results & Discussion

The IR spectra data represented in Table 1 is quoted as a copy-book example of the stretching vibrations of N-H bonds.These bands are broad and lie in the region of 3150-3290 cm^{-1} which are characteristic of the intermolecular hydrogen bonding N-H,Compaired with sharp absorption at 3430 $cm^{-1}$of the free N-H stretching frequency which has been observed in the IR spectra of compounds HI-(1,2,3,4,5).The stretching vibration of C=N bonds are located in the region of 1600-1635 cm^{-1} which are consistent with previous findings from other benzylidenes Schiff bases IR spectra[1,10].

The physical properties and thermogravimetric analysis of compounds HI-(1,2,3,4,5) are sumarised in Table 2.These compounds have almost followed the same thermal fragmentation pathway.The thermogravimetric curves for compounds HI-1 Fig.1 ;HI-3 Fig.3 ;HI-5 Fig.5 and HI-4 Fig. 4 show that the degradation of these compounds be at carbon-nitrogen bond,so they lost initially one thired and half the mass (76 mass unit) as NC-C≡C-CN at 244.2 ^{0}C , 234.3 ^{0}C, 274.8 ^{0}C and 227.8^{0}C respectively.Whereas the thermogravimetric curve of compound HI-2 Fig.2 shows that compound decomposed at phenyl-CH bond and it lost initially about half the mass (121 mass unit) as $C_6H_5N(CH_3)_2$ at 232.9 ^{0}C.The fragmentation patterns of compounds HI-(1,2,3,4,5)shown in Scheme 2.Compounds HI-1and HI-5 decomposed further above 593.2 ^{0}C and 660^{0}C up to 100 % respectively,on the other hand compounds HI-2, HI-3 and HI-4 were fragmented out, at higher temperature, up to 96.28 % , 78 % and 84.83% respectively .No attempt has been done to identify the residue of HI-2 (3.7% ;0.00004 g) , HI-3 (21% ;0.0006 g) and HI-4 (15% 0.0003 g) ,owing to their extermely small amounts.Our suggested mechanism for the thermal decomposition of compound HI-1 , HI-3 and

HI-5 is reasonable since it is well known that the reaction of aliphatic diamine with benzylidehyde yields benzylidene derivatives throughout the formation Schiff bases intermediates [15],a structure similar to HI-(1,2,3,5).

Table 1:Assignment of the majer IR absorption peaks of compounds HI-(1,2,3,4,5) spectra measured as KBr discs.

compound	free γaaz N-H	bended γ N-H	γ C≡N	γ C=N	δ N-H	γ C-N
HI-1	3430	3335,3325 3095	2200	1635	1605	1355
HI-2	3450,3410	3290,3150	2220,2190	1600	1570	1375
HI-3	3400	3290	2230,2190	1600	1570	1370
HI-4	3430	3360,3340	2200	1630	1610	1355
HI-5	3430	3290	2230,2190	1610	1585 1505	1385

γ :stretching frequency ; δ :bending frequency

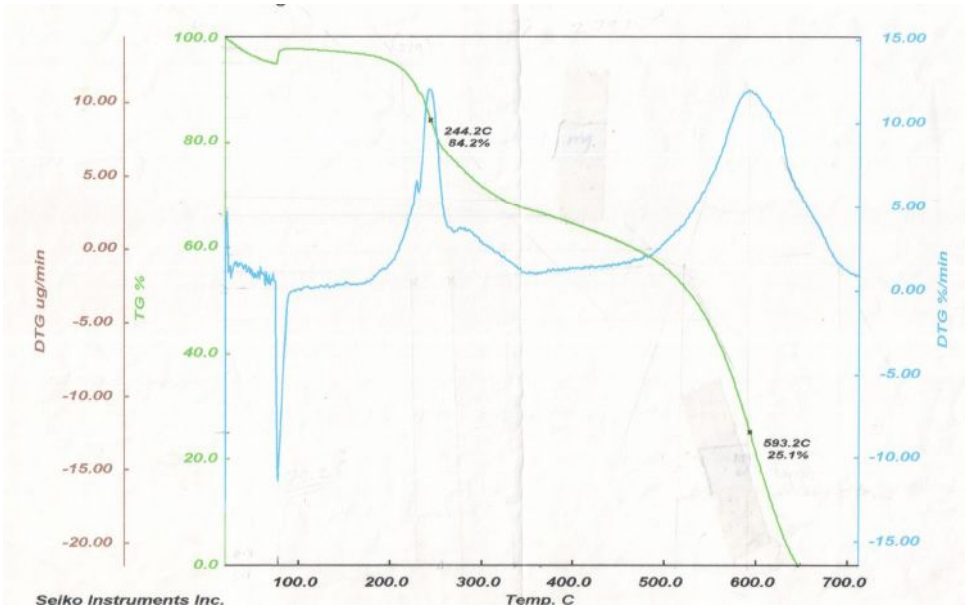


Figure 1:Thermogravimetric curve TG and DTG for compound HI-1.

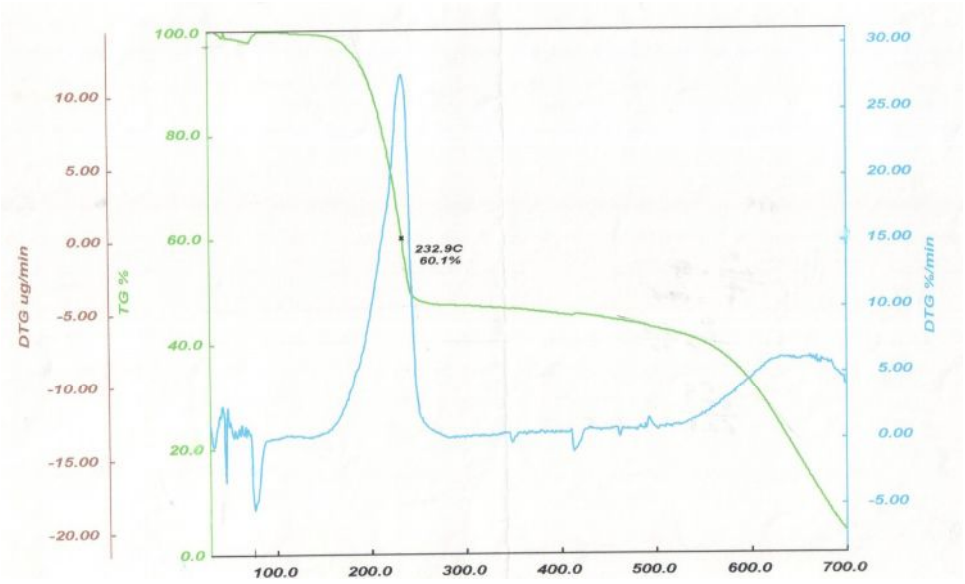


Figure 2:Thermogravimetric curve TG and DTG for compound HI-2.

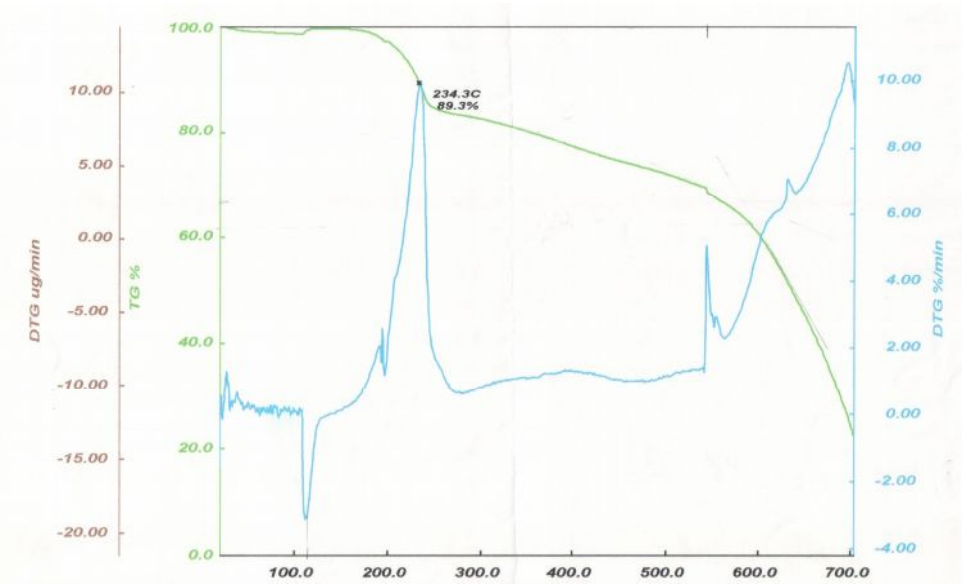


Figure 3:Thermogravimetric curve TG and DTG for compound HI-3.

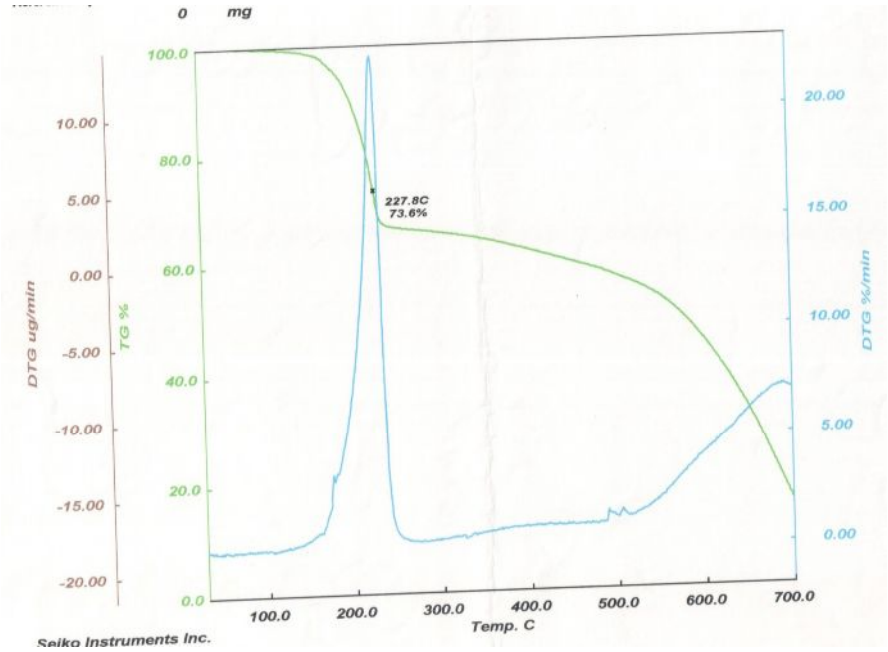


Figure4: Thermogravimetric curve TG and DTG for compound HI-4.

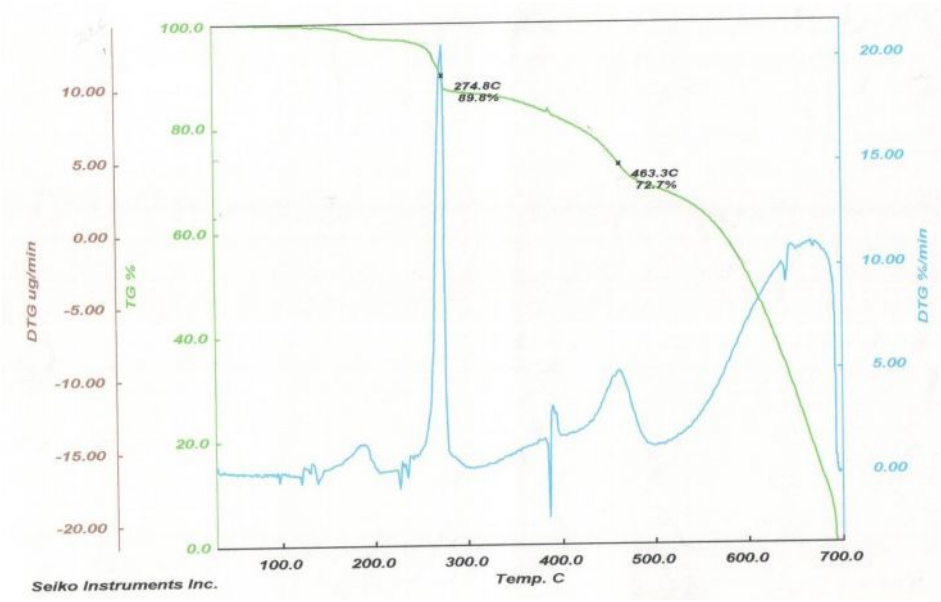
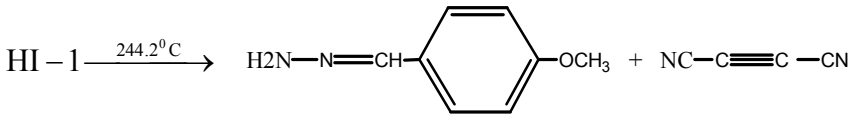
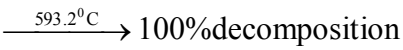


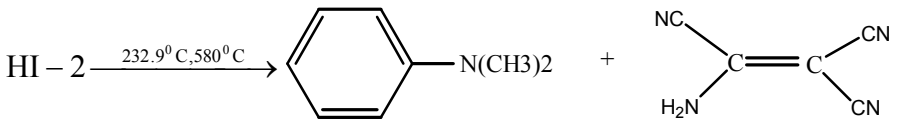
Figure5: Thermogravimetric curve TG and DTG for compound HI-5



%Calcu.: 33.6

%Found: 33.8



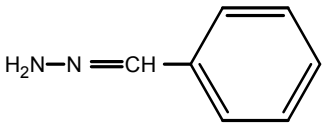
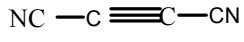


%Calcu.: 50.62

%Found: 50.37

$\xrightarrow{700^0\,C}$ 96.28 % decomposition

(0.04 mg residue)

HI – 3 $\xrightarrow{234.3^0\,C,532^0\,C}$  + 

%Calcu.: 38.8

%

Found:38.3

$\xrightarrow{688^0\,C}$ 78 % decomposition

(0.63 mg residue)

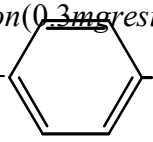
HI – 4 $\xrightarrow{227.8^0\,C,576^0\,C}$

H2N-N=CH-CH2CH2CH3 + NC-C≡≡C-CN

%Calc.:46.91

%Found.:46.61

$\xrightarrow{700^0}$ 84.83%*decompsition*(0.3*mg residue*)

HI – 5 $\xrightarrow{274.8^0\,C,463.3^0\,C}$ H2N=CH-  + NC-C≡C-CN

%Calc.:31.53

%Found.:31.57

$\xrightarrow{660^0\,C}$ 100%*decomposition*

Scheme 2

Table 2:The physical properties and thermogrvimetric analysis of compounds HI-(1,2,3,4,5).

compound	colour	m.p ^{0}C	M. wt	Initial wt (mg)	Initial lost Temp.^{0}C % wt	Residue (mg)
HI-1	Yellow-Lamin crystal	73-75	226	1.07018	244.2 84.2 %	----
HI-2	Yellow powder	60-62	239	1.07601	232.9 60.1 %	0.04
HI-3	Pale-Yellow Brilliant Crystal	110-112	196	2.92421	234.3 89.3 %	0.63
HI-4	Brown-Crystal	121	162	2.02757	227.8 73.6 %	0.3
HI-5	Turmeric Crystal	over 350	241	1.45463	274.8 89.8 %	----

References

Al-Hussain A.K.A.,(1997),spectral study of charge transfer complexes of some new B-keto Schiff bases and Schiff bases derived from 1,2-Diamino-2-propanol ,Ph.D.Thesis,University of Baghdad.

Al-Razag K.A.A.,(1997),spectral studies of some new Schiff bases and their complexes,Ph.D.Thesis ,University of Baghdad.

Benzylidenes)-1,3-diamine-2-propanol,Iraqi J.Chem.,18(1):41.

Grimmett M.R.in Sammes P.G.(Ed.)comprehensive organic chemistry, Hetrocyclic compounds ,pregaman press vol.4:398.

Saeed A.A.H.,(1993),thermal fragmentation of some Bis(p-substituted

Saeed A.A.H.,(1993),thermal fragmentationof some bis(p-substituted benzylidenes)-1,3-diamino-2-propanol,Iraqi J.Chem.18:41.

Saeed A.A.H.,Abbo H.S.,Haddad H.H.and Mattti G.Y.(1985),UV-Vis. spectrophotometric determination of microgram quantities of iron using new Schiff bases derived from 2,2/-Dipyridyl ketone, Can J.Spectrosc. 30:63.

Saeed A.A.H.,Ebraheem A,K and Abbas H.H.(1994),spectral characterization of some new disubstituted Bis(Benzylidenes)-1,3-diamine-2 Propanol,Iraqi J.Chem.19(1):41.

Saeed A.A.H.,Ebraheem E.K. and Abbas H.H.,(1993),thermal decomposition and mass fragmentation of some new Schiff bases, Spectrosc.letts.25(6)777.

Saeed A.A.H.,Ebraheem E.K. and Tossonian A.A.,(1986),thermal decomposition and mass fragmentationof some new hydroxyl Schiff bases,Thermochimmica Acta 97:337-343.

Saeed A.A.H.,Ebraheem E.K.and Abbas H.H.,(1994),thermal fragmentation of some substituted Bis(benzylidenes)-1,3-diamino-2-Propanol,Iraqi J. Chem.,19:175.

Saeed A.A.H.and Ebraheem E.K.(1983),A spectroscopic study of the trantomerism of new 3,1-Benzoxazines,Can J.spectrosc.28:169.

Saeed A.A.H.and Ebraheem E.K.(1983),preparation of phenylquinoxaline from α,α-Diaminoketon and Dimethyl-o-phenylenediamine,J.Hetro.Chem.20:1739.

Saeed A.A.H.and Matti G.Y.(1979),kinetics & spectroscopic investi-gations of the reactions of methyl iodide with benzylidene-p-N,N-dimethylaminoaniline,Indian J.Chem.18B:338-340.

Shareef A.M.,(1994),spectrophotometric study of charge transfer complexes between some Schiff bases and a number of electronic acceptors in chloroform,Ph.D.Theses,University of Baghdad.

Willi A.V.and Siman J.F.,(1968),kinetics of hydrolysis of O-methyl Benzylideneaniline and O-hydroxybenzylideneaniline,Can Chem. 46:1589.