THERMAL BEHAVIOR OF SOME NEW PHENOXYALKYL CARBOXYLIC ACIDS DERIVATIVES IN NITROGEN ATMOSPHERE

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Abstract: In the present paper new compounds are characterized by TG-DTG-DTA thermal methods in order to investigate the structure-thermostability-degradation mechanism correlation. The results of thermal analysis are indicative of a complex degradation mechanism which is characteristic of every sample, some similarities reflecting the structure influence being also noticed.
The initial degradation temperatures resulting from TG-DTG-DTA led to the estimation of the temperature range of using and storing these compounds which is an useful information if their possible practical applications and of some derivatives as herbicides, plant growth stimulators, fungicides, acaricides are taken into account. Apart from this, the presence of the diazo and azo group in the structure of these new compounds could make possible some useful applications for dying of proteic fibres.

Keywords: *azomethine, diazoaminoderivatives, thermal analysis (TG-DTG-DTA), thermostability, action mechanism.*

INTRODUCTION

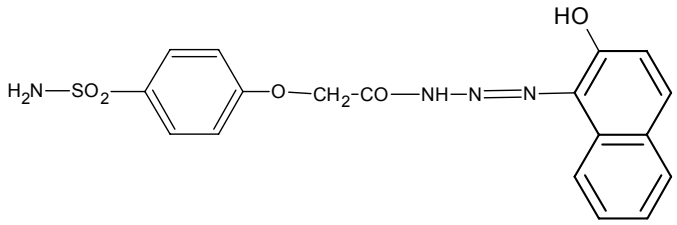
By carrying on our previous studies in this field [1, 2], the present paper is devoted to the synthesis and thermal characterization by TG-DTG-DTA thermal methods [2 – 5] of two new diazoaminoderivatives, 1-(3-{2-[4-(aminomethyl)-phen-oxy]ethyl}triaz-1-enyl)-2naphthol **(1)**, 8-(3-{2-[4-(aminomethyl)-2-methilphenoxy]ethyl}triaz-1-enyl)-2-hydroxy-1-naphthoic acid **(2)** and one new azomethine 4-nitrobenzaldehide-{2-[2-(sulphonamido)-4-chloro-phenoxy]ethyl}hydrazone **(3)**, under nitrogen atmosphere, in order to follow the structure-thermostability-degradation mechanism correlation.
The quantitative analysis by TG-DTG under nitrogen atmosphere afforded a discussion on the thermal degradation mechanism.
The compounds under study were found to suffer a thermal degradation into two stages, the first one being the most significant.
The melting temperatures estimated by both DTA [6 – 9] under nitrogen atmosphere and Boetius method were in good agreement.

EXPERIMENTAL

The synthesis optimum conditions as well as the elemental analysis data and the NMR spectral measurement confirmed the formation of the corresponding new compounds, azomethine and diazoaminoderivatives [10 – 13].
The mention has to be made that these compounds were separated with acetone as a solvent.
In Figure 1 the structures of the obtained azomethine and diazoaminoderivatives, their chemical formulae, denominations, molecular weights, and melting points measured by the Boetius method are given.

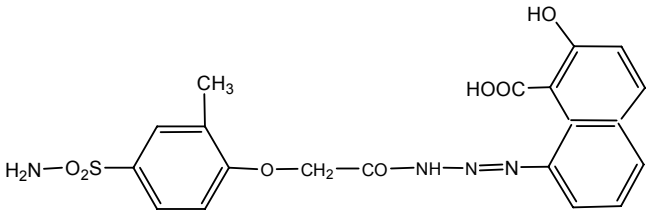
Thermal analysis

The thermogravimetric (TG) and differential thermal analysis (DTA) were performed by using a Perkin-Elmer Pyris Diamond TG/DTA thermobalance which records simultaneously the T, TG and DTA curves. The DTG curves were obtained by numerical differentiation of the TG curves. The working conditions were the following: sample mass: 12 mg, heating rate: 10 ^{0}C.min^{-1}, temperature range: 30 – 900 ^{0}C in nitrogen stream (800 mL.min^{-1}).



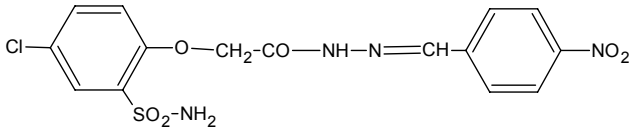
1-(3-{2-[4-(aminomethyl)phenoxy]ethyl}triaz-1-enyl)-2-naphthol **(1)**

Chemical formula: $C_{18}H_{16}N_4O_5S$
Molecular weight: 400
Melting point: 224 – 225 ^{0}C



8-(3-{2-[4-(aminomethyl)-2-methilphenoxy]ethyl}triaz-1-enyl)-2-hydroxy-1-naphthoic acid **(2)**

Chemical formula: $C_{20}H_{18}N_4O_7S$
Molecular weight: 458
Melting point: 216 – 218 ^{0}C



4-nitrobenzaldehide {2-[2-(sulphonamido)-4-chlorophenoxy]ethyl}hydrazone **(3)**

Chemical formula: $C_{15}H_{13}O_6\ N_4SCl$
Molecular weight: 412.5
Melting point: 229 – 234 ^{0}C.

Figure 1. *Samples under study (structure, molecular weight and melting points)*

RESULTS AND DISCUSSION

The TG, DTG şi DTA curves of the compounds presented in Figure 1 are depicted in Figures 2 – 4.

The examination of the TG and DTG curves allows the conclusion that the thermal degradation mechanism, under nitrogen atmosphere, is specific and complex under the given working conditions, a similarity of the samples under study being noticed.

The diazoaminoderivatives under investigation were found to decompose into two stages, the first one being significant. The DTG curves show in this stage a clear

inflexion point on compound (**1**) while the sample (**2**) is seen to show two separated processes as revealed by the two curve maxima.

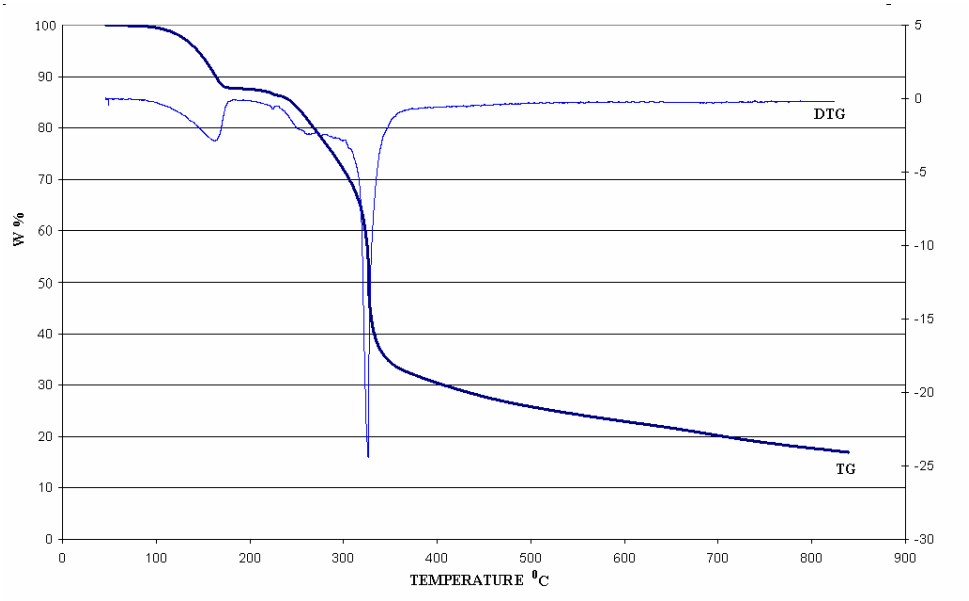


Figure 2. *TG and DTG curves of the compound (**1**)*

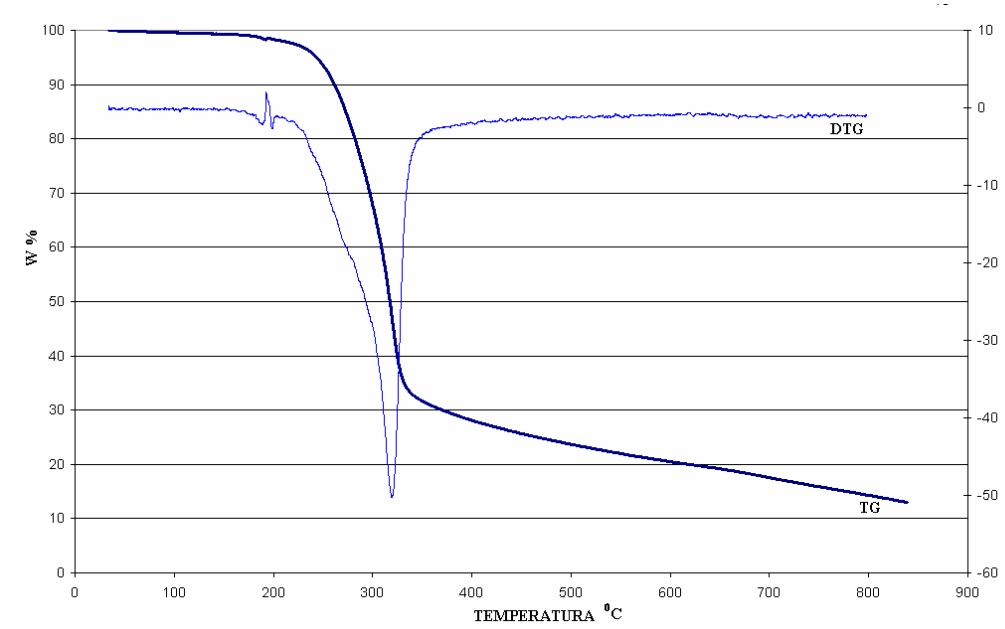


Figure 3. *TG and DTG curves of the compound (**2**)*

In Table 1 the characteristic amounts resulting from TG – DTG are given: T_i, °C = initial degradation temperature; T_{inf}, °C = temperature corresponding to the inflexion point of the descending branch of the DTG curve; T_m, °C = temperature corresponding to the maximum degradation rate; T_f,°C = final degradation temperature; $W\infty_{inf}$%, $W\infty$ % = weight losses at the inflexion temperature, respectively, as well as resulting residue (%).

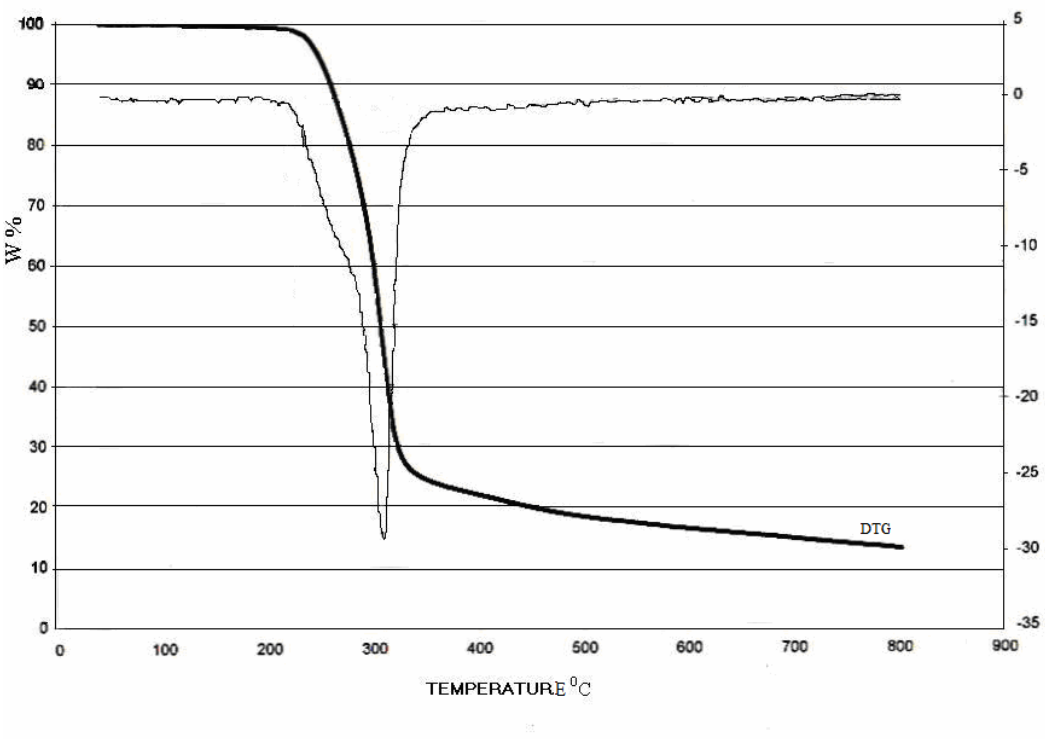


Figure 4. *TG and DTG curves of the compound* ***(3)***

Table 1*. Characteristic amounts from TG-DTG curves*

Stage	Parameter	Compound		
		1	**2**	**3**
Stage I	T_i	211.2	195.72	220.32
	T_{inf}	314.44	263.83	280.38
	$W_{\infty inf}$	20.13	18.01	18.68
	T_m	330.24	282.75 290.29	306.0
	T_f	380.16	371.34	357.0
	W_∞	34.32	69.96	42.83
Stage II	T_i	380.16	371.34	357.0
	T_m	900	900	900
	W_∞	45.55	12.03	26.78
Residue	*%*	15.51	11.22	11. 71
	Color	brown	reddish	white

As revealed by the data from Table 1, the first degradation stage, which is the significant one, develops within the 175.36 – 380 ^oC temperature range while the second proceeds between 380 – 900 ^oC.

The thermal stabilities of the samples expressed by T_i - initial temperature of thermal degradation under nitrogen atmosphere led to the following series: **3 > 1 > 2**.

A discussion on the stabilities of the three compounds under study by taking the electronic effects into account results in the following conclusions:

The main factor determining the stability of the three compounds is the electron-releasing effect (+E) of the ethereal oxygen. This effect is responsable for the electronic delocalization in the aromatic ring resulting in the double bond character given to the C–S bond which means that the higher the (+E) effect of the ethereal oxygen the higher the C–S bond order and the compound stability.
In case of the compound (**1**), the effect (+E) of the ethereal oxygen brings a contribution to the electronic delocalization in the aromatic ring and thus to the increase of the C–S bond strength to a second order bond, this compounds being more stable than the derivative (**2**).
The compound (**2**) contains a chlorine atom substituted in different positions towards the sulphonamidic group (S–C) in their aromatic ring. The chlorine atom showing a strong (–I) effect causes the stopping of the electronic delocalization in the aromatic ring at the carbon atom linked to the chlorine atom which results in the decrease of the C–S bond order and hence of the thermal stability of these compounds.
Since the –C=N– bond in the azomethine (**3**) is more stable than the –N=N– bond in the diazoaminoderivatives (**1**) and (**2**) it follows that the compound (**3**) is more stable than the compounds (**1**) and (**2**). This compound being more stable than the derivatives (**1**) and (**2**).
The fact is thus made evident that the thermal stabilities of the three diazoaminoderivatives obey the same series found by means of the TG-DTG-DTA thermal analysis: **3 > 1 > 2**.
It can be noticed that the obtained values are close to the theoretical ones for this bond type.

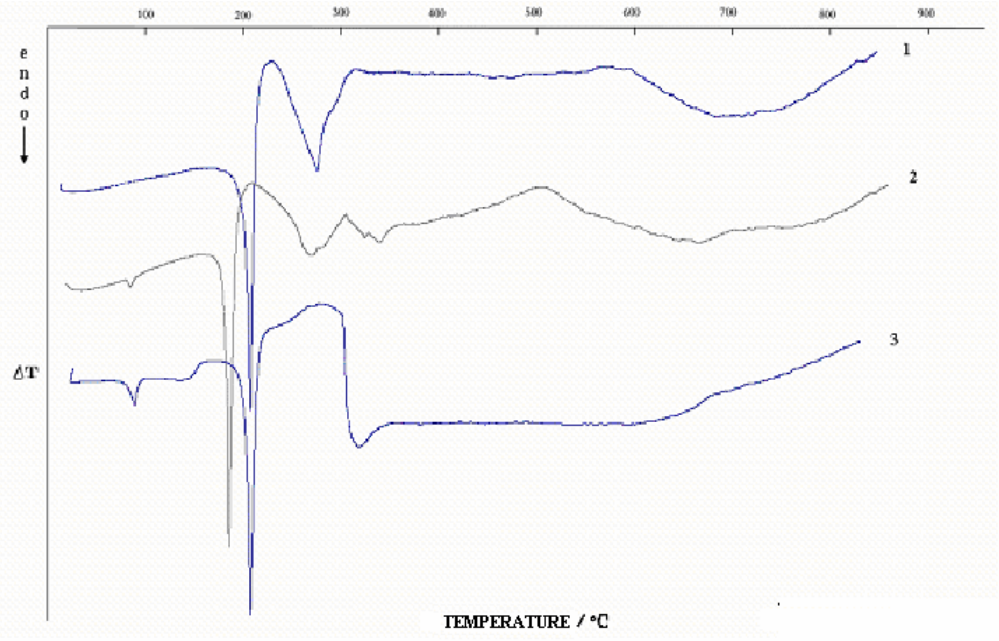


Figure 5. *DTA curves of the samples (**1**), (**2**), (**3**).*

The analysis of the DTA curves confirms the complex and specific mechanism resulting from the TG-DTG analysis, the same well-defined endothermic degradation stages

being made evident. The compounds show prior to the thermal degradation stages an endothermal peak within the 178 – 257 ^{o}C temperature range where the sample weights (TG-DTG) are constant corresponding to the melting peak.
The characteristic temperatures from DTA are given in Table 2.

Table 2. *Characteristic temperatures from DTA*

Sample	Melting			Stage I			Stage II		Thermal nature
	T_i	T_m	T_f	T_i	T_m	T_f	T_i	T_f	
(**1**)	199.68	224.64	257.28	257.28	318.72	364.80	364.80	900	endo
(**2**)	178.16	219.18	231.11	231.11	279.89	310.02	310.02	900	endo
(**3**)	208.08	228.48	248.88	248.88	297.84 314.16	332.52	332.52	900	endo

The data in Table 2 indicate the same degradation temperature range as resulted from the TG-DTG: 188 – 900 ^{o}C. The existence of two processes in the first degradation stage is made evident in DTA by the presence of two endothermic peaks, the former corresponding to the NH_2–SO_2– group elimination since the inflexion temperatures in TG-DTG correspond to the temperatures at the maximum of the first peak of the DTA curve.
For the second degradation process of the first stage the temperatures at the DTA peak maximum coincide with those in DTG at the maximum degradation rate which also supports the two chemical processes developing during the first stage.
The melting temperatures were estimated from the temperatures corresponding to the maximum of the DTA peak [7].
In table 3, the melting points of the samples estimated by both Boetius method and DTA are given which indicates the good agreement of the values thus obtained.

Table 3. *Melting temperatures[°C]*

Sample	DTA method	Boetius method
(**1**)	224.64	224 – 225
(**2**)	219.18	216 – 218
(**3**)	228.48	229 – 234

CONCLUSIONS

The analysis of the TG–DTG–DTA curves of the compounds under study is indicative of a complex and specific mechanisms of thermal degradation, confirming the structure influence.
The elucidation of the behavior of the newly synthesized compounds would be useful for their characterizations if the possible applications as agrochemicals or as dyes are taken into account.
The thermal stabilities of the investigated compounds estimated by DTG and DTA methods obey the following series: **3 > 1 > 2**.
The melting points of the complexes estimated from DTA were in good agreement with those measured by the Boetius method.

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