

## Synthesis and Thermal Analysis of Some Ferrocene Derivatives

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*(Received 19 September 2010, Accepted 21 December 2010)*

This paper presents the synthesis and the thermal behavior of some symmetrical derivatives containing two ferrocenyl units. The influence of the following factors upon the thermal stability was estimated: the degradation atmosphere, the nature of the linking groups, the number of the benzene units and the flexible segment position.

**Keywords:** Synthesis, Ferrocene derivatives, Thermal analysis, Structure-thermostability relationship

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### INTRODUCTION

The physical and chemical properties of materials are mainly determined by the functional unit combinations existing within their structure. Organometallics combine the properties of transition metal elements into organic frame works providing access to a range of properties and geometries which are denied to other organic compounds [1-5]. For designing new organometallic materials which display thermotropic liquid crystalline behavior, the thermal stability of a newly synthesized compound is an important feature which affects its practical applications, especially in fields where high temperature processing or operation is required. Thus, thermal analysis methods (TG/DTG/DTA) are frequently employed in the rational design of such materials [6-10]. Ferrocene may be readily functionalized with a variety of mesogenic and promesogenic moieties in order to obtain materials with liquid crystalline phases. Metallomesogens often display high melting and isotropization temperatures

associated with the increased strength of intermolecular interaction. Ferrocene is a three-dimensional unit that, when derivatized with mesogenic units, can cause steric repulsion effects towards the neighboring molecules.

This effect has been shown to decrease the transition temperatures of materials to enable them to exhibit liquid crystalline properties at low temperature. In addition to this, the destabilization of the crystalline phase also results in decreased isotropization temperatures making ferrocene an attractive component in the design of room temperature thermotropic metallomesogens [11-20].

In this paper, we report the synthesis and thermal analysis of a series of symmetric ferrocene-containing compounds in which the mesogenic moieties are connected *via* estheric, iminic or azo units.

The thermal stability was investigated through thermogravimetric studies (TG, DTG and DTA). Two sets comprising compounds were synthesized to investigate the effect of both aliphatic aromatic fraction and the directionality of linkage units on the liquid crystalline properties of this class of compounds. Surprisingly, a liquid crystalline (LC) phase

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was observed in only one compound and not in its structural analogues. The absence of mesomorphic properties in all the other compounds may be due to the short length of the mesogenic units, causing intermolecular interactions that are too weak to allow of liquid crystal type ordering. Also, the presence of two ferrocenyl units may overwhelm the effect of the mesogenic units.

## EXPERIMENTAL

### Material

The symmetrical ferrocene derivatives with two ferrocenyl units, including either a peripheral or a central flexible unit, were obtained by esterification of the ferrocene containing acids with a promesogenic bis-phenol, in the presence of DCC/DMAP, or by condensation of ferrocene containing amines with an dialdehyde. The structure of the resulting compounds was confirmed by NMR, IR and mass spectroscopy. The synthetic routes are presented in Schemes 1 and 2.

The design of the ferrocene derivatives reported here allows of the analysis of the influence of the following

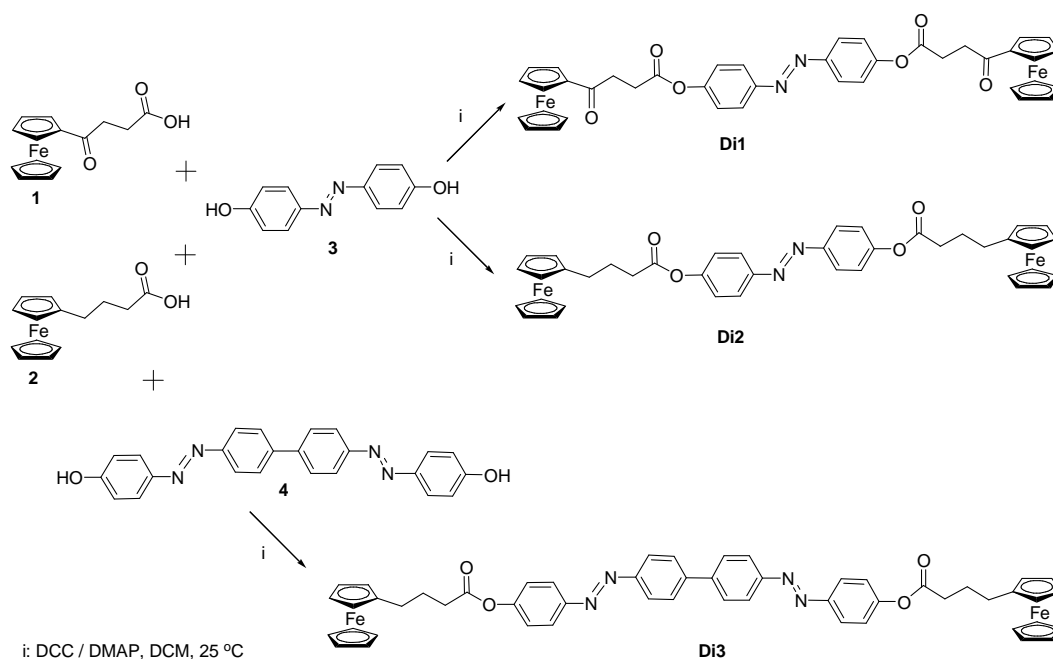
structural parameters upon the thermal stability: the nature and directionality of the linking groups, the number of aromatic units and the position of the flexible spacer.

### Synthesis

Derivatives **Di1-Di3** were synthesized by esterification of the ferrocenyl acids **1**, **2** with the corresponding bis-phenols **3**, **4** according to the following general procedure

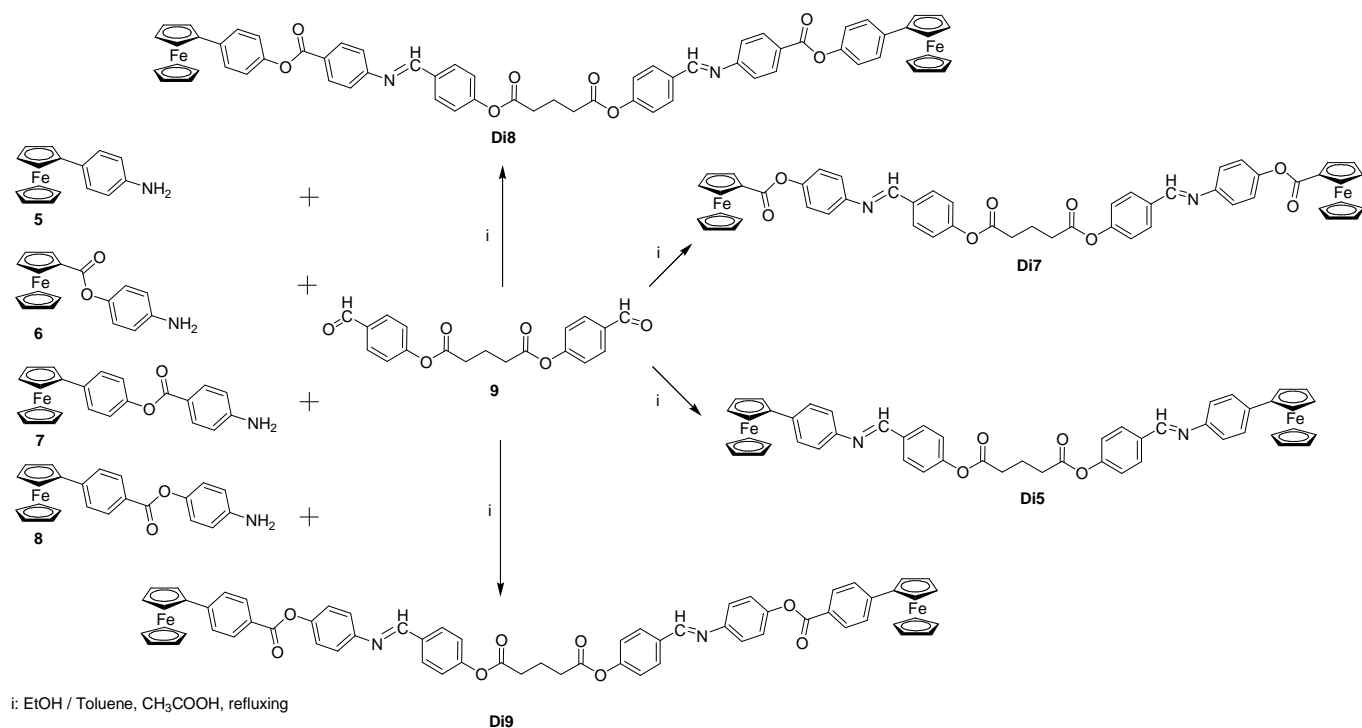
Ferrocene acid (2 eq), bis-phenolic mesogen (1 eq), a catalytic amount of DMAP and dry DCM were stirred for 10 min under a flow of nitrogen. To this solution, 2.2 eq of DCC dissolved in the minimum amount of dry DCM was added at once and the reaction mixture was stirred for 24 h at rt, under a flow of nitrogen, whereupon the dicyclohexyl urea was filtered off and the solution was concentrated. The crude material was purified by column chromatography on silicagel with the appropriate mixture of solvents.

**4,4'-Bis-(4-ferrocenyl-4-oxobutanoyloxy)azobenzene (Di1)**. Quantities: 0.5 g (1.74 mmol) derivative **1**, 0.18 g (0.86 mmol) compound **3**, DMAP, 0.395 g (1.9 mmol) DCC, 50 ml CH<sub>2</sub>Cl<sub>2</sub>, purification: CH<sub>2</sub>Cl<sub>2</sub>:ethyl acetate (15:1), 0.57 g (87.5%); <sup>1</sup>H NMR δ<sub>H</sub> (CDCl<sub>3</sub>): 7.93 (d, 4H, Ar), 7.29 (d, 4H,



Scheme 1. The synthesis of the symmetrical ferrocene derivatives with flexible peripheral units

## Synthesis and Thermal Analysis of Some Ferrocene Derivatives



Scheme 2. The synthesis of the symmetrical ferrocene derivatives with a central flexible core

Ar), 4.82 (t, 4H, ferrocene), 4.51 (t, 4H, ferrocene), 4.23 (s, 10H, ferrocene), 3.19 (t, 4H, -CH<sub>2</sub>-), 2.95 (t, 4H, -CH<sub>2</sub>-); <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>): 201.76, 171.47, 152.89, 150.19, 124.09, 122.32, 78.26, 72.36, 70.05, 69.25, 34.22, 28.2.

**4,4'-Bis-(4-ferrocenylbutanoyloxy)azobenzene (Di2).** Quantities: 0.5 g (1.8 mmol) compound **2**, 0.19 g (0.91 mmol) compound **3**, DMAP, 0.41 g (2.01 mmol) DCC, 50 ml CH<sub>2</sub>Cl<sub>2</sub>, purification: CH<sub>2</sub>Cl<sub>2</sub>, 0.45 g (67.7%), <sup>1</sup>H NMR δ<sub>H</sub> (CDCl<sub>3</sub>): 7.94 (d, 4H, Ar), 7.23 (d, 4H, Ar), 4.11-4.07 (m, 18H, ferrocene), 2.60 (t, 4H, -OCO-CH<sub>2</sub>-), 2.47 (t, 4H, -CH<sub>2</sub>-COO), 1.96 (cv, 4H, C-CH<sub>2</sub>-C), <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>): 171.65, 152.75, 150.1, 124.06, 122.21, 77.22, 68.54, 68.15, 67.33, 33.92, 28.94, 26.13.

**4,4'-Biphenyl-4,4'-diylbis(diazene-2,1-diyl)bis(4,1-phenylene) bis(4-(ferrocenyl)butanoate)(Di3).** Quantities: 0.4 g (1.47 mmol) derivative **2**, 0.28 g (0.73 mmol) derivative **4**, DMAP, 0.33 g (1.67 mmol) DCC, 50 ml CH<sub>2</sub>Cl<sub>2</sub>, purification: CH<sub>2</sub>Cl<sub>2</sub>, 0.35 g (26.4%), <sup>1</sup>H NMR δ<sub>H</sub> (CDCl<sub>3</sub>): 8.01 (d, 4H, Ar), 7.98 (d, 4H, Ar), 7.74 (d, 4H, Ar), 7.25 (d, 4H, Ar), 4.11-4.0 (m, 18H, ferrocene), 2.61 (t, 4H, -CH<sub>2</sub>-),

2.47 (t, 4H, -CH<sub>2</sub>), 1.97 (cv, 4H, CH<sub>2</sub>), <sup>13</sup>C NMR δ<sub>C</sub> (CDCl<sub>3</sub>): 171.68, 152.79, 152.01, 150.28, 142.63, 127.86, 124.13, 124.11, 123.49, 122.23, 87.77, 77.22, 68.57, 68.15, 33.92, 28.94, 26.13.

Derivatives **Di5**, **Di7**, **Di8** and **Di9** were synthesized by condensation of the ferrocenyl amines **5** + **8** with the di-aldehyde **9** in the presence of a catalytic amount of acetic acid according to the general procedure described below. To a stirred solution containing the ferrocenyl amines (2 eq) and the di-aldehyde **9** (1 eq) dissolved in ethanol or toluene were added a few drops of glacial acetic acid. The solution was heated at reflux, under stirring for 4-7 h and allowed to cool to rt. The Schiff base precipitates from solution and the resulting red precipitate was filtered out and washed with cold ethanol or toluene. The brick red powder was recrystallized from ethanol or purified by column chromatography on silica with the corresponding eluent.

**Bis(4-(4-(ferrocenyl)phenylimino)methyl)phenyl glutarate (Di5).** Quantities: 0.3 g (0.88 mmol) compound **9**, 0.488 g (1.76 mmol) derivative **5**, 20 ml EtOH, acid acetic

(catalytic), refluxing 4 h, recrystallized from EtOH, 0.13 g (18.09%),  $^1\text{H NMR } \delta_{\text{H}}$  ( $\text{CDCl}_3$ ): 8.50 (s, 2H, -CH=N-), 7.94 (d, 4H, Ar), 7.49 (d, 4H, Ar), 7.22 (d, 4H, Ar), 7.17 (d, 4H, Ar), 4.64 (t, 4H, ferrocene), 4.31 (t, 4H, ferrocene), 4.04 (s, 10 H, ferrocene), 2.77 (t, 4H,  $\text{OCOCH}_2$ ), 2.22 (cv, 2H, C- $\text{CH}_2$ -C),  $^{13}\text{C NMR } \delta_{\text{C}}$  ( $\text{CDCl}_3$ ): 170.99, 157.88, 152.77, 149.4, 137.49, 134.17, 129.91, 126.73, 121.97, 121.07, 72.21, 70.79, 70.12, 68.10, 33.25, 20.32.

**Bis(4-(4-(ferrocenecarbonyloxy)phenylimino)methyl)phenyl glutarate (Di7).** Quantities: 0.15 g (0.44 mmol) derivative **9**, 0.28 g (0.88 mmol) derivative **6**, 15 ml toluene, 2 drops of acetic acid, refluxing 7 h, recrystallized from toluene, purification cc  $\text{CH}_2\text{Cl}_2$ :hexane:TEA (1:1:3%), 0.119 g (29.8%),  $^1\text{H NMR } \delta_{\text{H}}$  (DMSO): 8.70 (s, 2H, -CH=N-), 8.03 (d, 4H, Ar), 7.39-7.29 (m, 12H, Ar), 4.95 (t, 4H, ferrocene), 4.64 (t, 4H, ferrocene), 4.38 (s, 10H, ferrocene), 2.80 (t, 4H, - $\text{CH}_2$ -), 2.06 (cv, 2H, C- $\text{CH}_2$ -C),  $^{13}\text{C NMR } \delta_{\text{C}}$  (DMSO): 171.8, 170.34, 160.46, 153.39, 149.34, 149.28, 134.26, 130.53, 123.3, 122.99, 122.63, 72.74, 70.87, 70.45, 69.35, 33.1, 20.12.

**Bis(4-(4-((4-(ferrocenylphenoxy)carbonyl)phenylimino)methyl)phenyl glutarate (Di8).** Quantities: 0.128 g (0.88 mmol) derivative **9**, 0.3 g (1.76 mmol) derivative **7**, 15 ml toluene, 2 drops of acetic acid, refluxing for 4 h, recrystallized from toluene, purification cc  $\text{CH}_2\text{Cl}_2$ :hexane:TEA (2:1:3%), 0.151 g (37.9%),  $^1\text{H NMR } \delta_{\text{H}}$  (DMSO): 8.70 (s, 2H, -CH=N-), 8.07-8.02 (m, 8H, Ar), 7.76 (d, 4H, Ar), 7.41-7.34 (m, 12H, Ar), 4.97 (t, 4H, ferrocene), 4.49 (t, 4H, ferrocene), 4.07 (s, 10 H, ferrocene), 2.81 (t, 4H, - $\text{CH}_2$ -), 2.06 (cv, 2H, C- $\text{CH}_2$ -C),  $^{13}\text{C NMR } \delta_{\text{C}}$  (DMSO): 171.81, 165.23, 160.58, 153.4, 149.52, 149.45, 146.77, 134.26, 131.68, 130.58, 130.55, 126.44, 123.3, 123.01, 122.64, 82.94, 70.64, 70.27, 67.54, 33.12, 20.12.

**Bis(4-(4-(4-(ferrocenyl)benzoyloxy)phenylimino)methyl)phenyl glutarate (Di9).** Quantities: 0.128 g (0.88 mmol) derivat **9**, 0.3 g (1.76 mmol) derivative **8**, 15 ml toluene, 2 drops of acetic acid, refluxing 5 h, recrystallized from toluene, purification cc with  $\text{CH}_2\text{Cl}_2$ :hexane:TEA (2:1:3%), 0.118 g (29.5%);  $^1\text{H NMR } \delta_{\text{H}}$  (DMSO): 8.71 (s, 2H, -CH=N-), 8.07-8.02 (m, 8H, Ar), 7.76 (d, 4H, Ar), 7.41-7.34 (m, 12H, Ar), 4.97 (t, 4H, ferrocene), 4.49 (t, 4H, ferrocene), 4.07 (s, 10H, ferrocene), 2.81 (t, 4H, - $\text{CH}_2$ -), 2.06 (cv, 2H, C- $\text{CH}_2$ -C),  $^{13}\text{C NMR } \delta_{\text{C}}$  (DMSO): 171.81, 165.23, 160.58, 153.42, 153.41, 149.53, 149.45, 146.77, 134.26, 131.69,

130.58, 130.55, 126.44, 126.32, 123.31, 123.01, 122.64, 77.94, 70.64, 70.27, 68.54, 52.57, 33.25, 20.15.

## Equipment

Thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA-SDTA 851e type derivatograph under a flow of nitrogen or air ( $20 \text{ ml min}^{-1}$ ), in the temperature range of  $25 \text{ }^\circ\text{C}$ - $900 \text{ }^\circ\text{C}$ , using a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  and a 4-6 mg of the sample weight. Constant operating parameters were kept for all the samples in order to obtain comparable data.

## RESULTS AND DISCUSSION

The thermogravimetric (TG) curves, their derivatives (DTG) and the differential thermal analysis (DTA) curves recorded during the analysis of the symmetrical derivatives containing two ferrocenyl units, using the Mettler Toledo derivatograph in inert atmosphere ( $\text{N}_2$ ) and in air are shown in Figs. 1 and 2.

The results indicate that complex degradation mechanisms, which occur in one to five decomposition steps, depend on the structure of the material and on the degradation atmosphere. In all the samples, the degradation did not decompose the whole sample, whether in nitrogen or in air. The remaining residue amount was between 17 and 53% of the sample weight which was larger than when the thermal degradation was performed in inert atmosphere.

The most important thermogravimetric parameters such as:  $T_{\text{onset}}$  -the temperature at which the thermal degradation begins,  $T_{\text{peak}}$  -the temperature at which the degradation rate reaches its maximum value,  $T_{\text{endset}}$  -the temperature at which the process ends, W% -the percentage weight loss in each step, the amount of residue and  $T_{\text{t}}$  -melting point are presented in Table 1.

In order to compare the thermal stability of the analyzed compounds, it was necessary to examine the  $T_{\text{c}}$  parameter, which is defined in Eq. (1), based on two essential thermal stability characteristics,  $T_{\text{onset}}$  and  $T_{\text{peak}}$  in the first decomposition step.

$$T_{\text{c}} = \frac{C_1 \cdot T_{\text{onset}} + C_2 \cdot T_{\text{Peak}}}{C_1 + C_2} \quad (1)$$

where  $C_1$  and  $C_2$  are coefficients related to the influence of the

Synthesis and Thermal Analysis of Some Ferrocene Derivatives

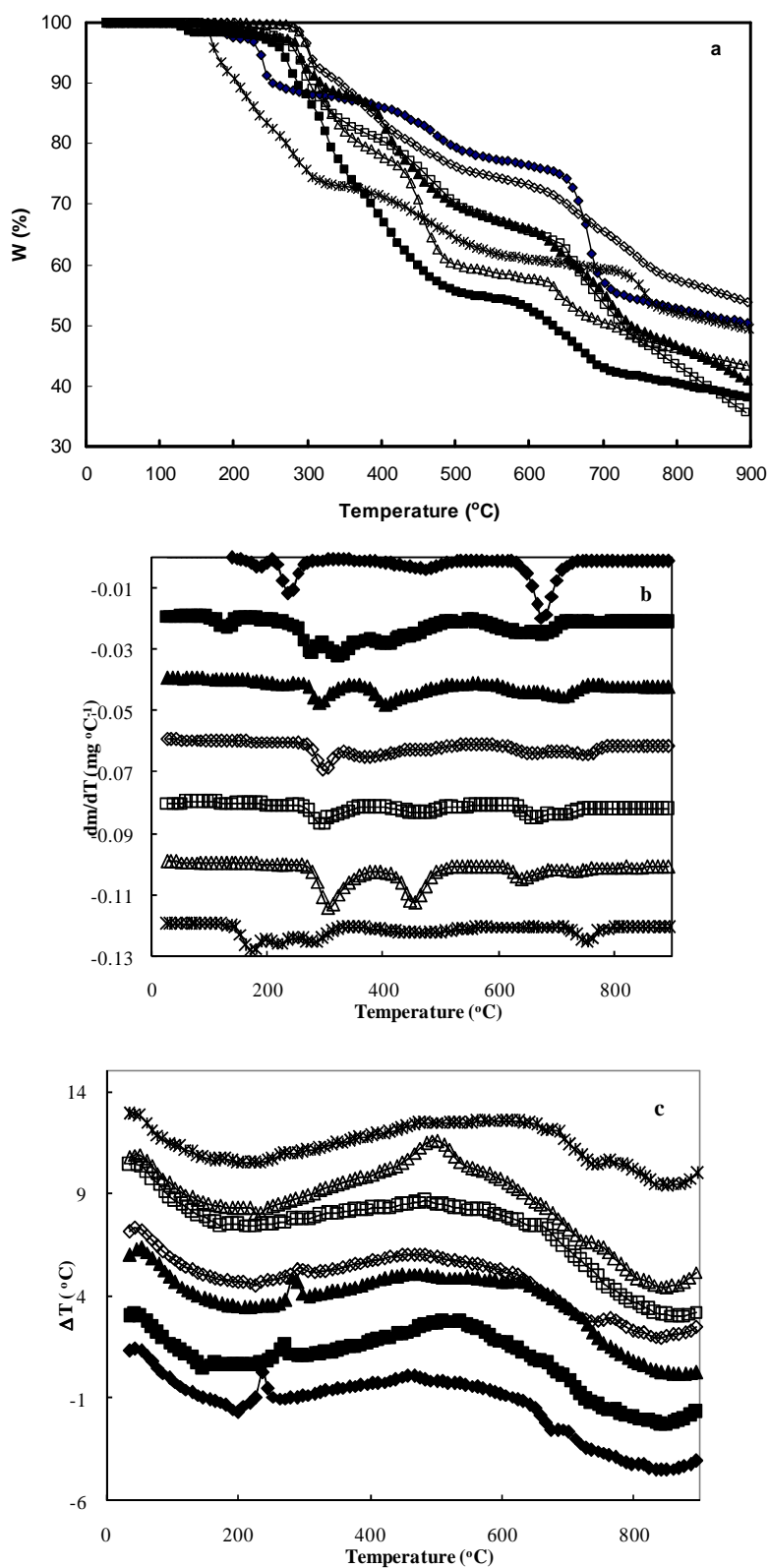
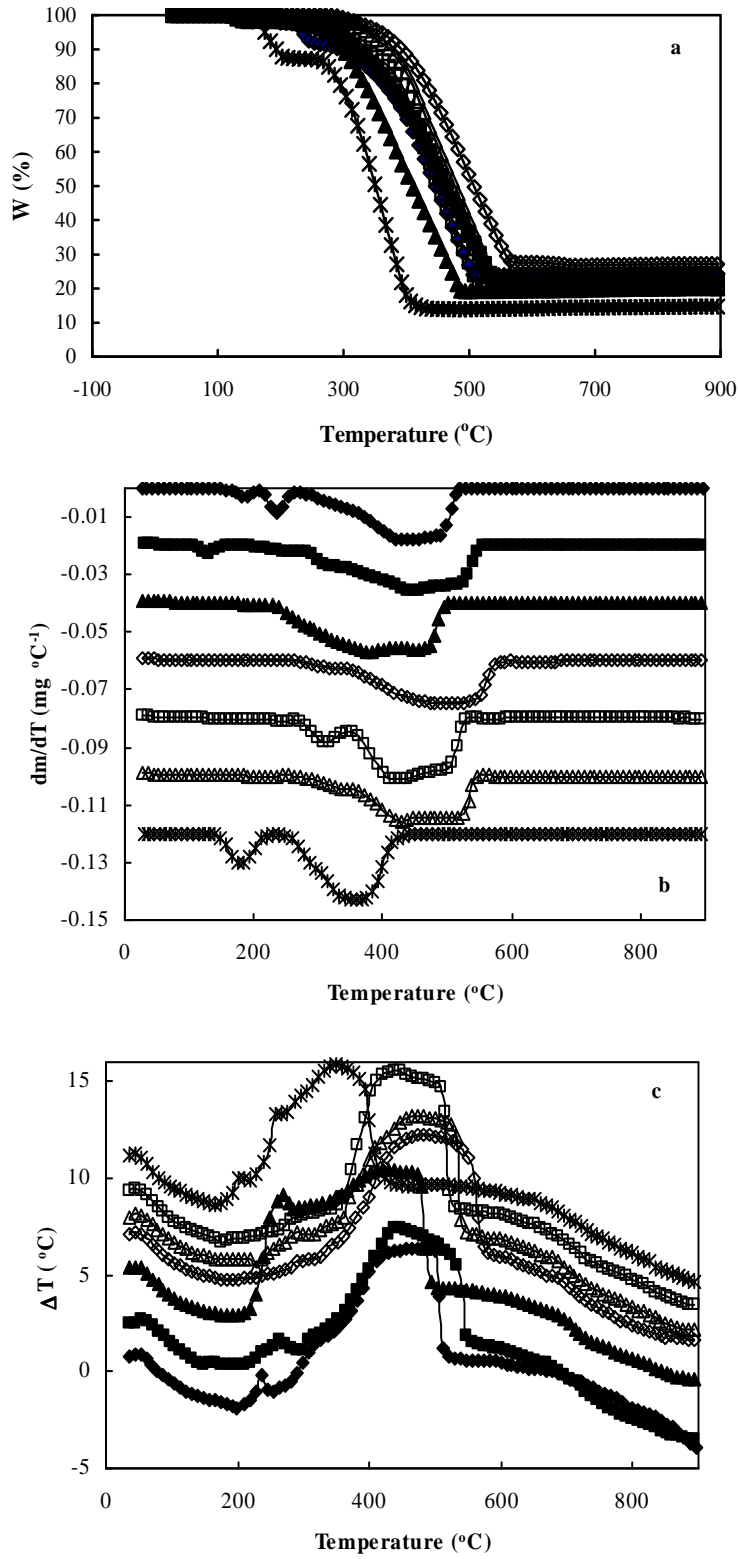


Fig. 1. Thermal analysis in nitrogen atmosphere (a) TG, b) DTG and c) DTA curves)

◆ Di1    ■ Di2    ▲ Di3    ◇ Di5    □ Di7    △ Di8    \* Di9



**Fig. 2.** Thermal analysis in air (a) TG, b) DTG and c) DTA curves)

◆ Di1    ■ Di2    ▲ Di3    ◇ Di5    □ Di7    △ Di8    \* Di9

## Synthesis and Thermal Analysis of Some Ferrocene Derivatives

**Table 1.** Thermogravimetric Parameters Recorded During the Analysis of the Symmetrical Derivatives with Two Ferrocenyl Units

Sample name	Melting point (T <sub>m</sub> , °C)	Stage	Nitrogen atmosphere				Air			
			T <sub>onset</sub> (°C)	T <sub>peak</sub> (°C)	T <sub>endset</sub> (°C)	W%	T <sub>onset</sub> (°C)	T <sub>peak</sub> (°C)	T <sub>endset</sub> (°C)	W%
<b>Di1</b>	201	I	174	188	194	2.58	170	189	195	2.35
		II	230	239	246	9.91	230	237	245	6.69
		III	398	475	509	10.98	314	464	506	68.57
		IV	648	679	708	26.96	-	-	-	-
		<i>Residue</i>				49.57				22.39
<b>Di2</b>	142	I	121	130	139	1.72	119	129	139	1.71
		II	265	276	311	13.49	217	260	298	3.82
		III	311	325	393	12.24	298	449	541	73.72
		IV	393	404	488	18.42	-	-	-	-
		V	590	685	701	16.91	-	-	-	-
		<i>Residue</i>				37.22				20.75
<b>Di3</b>	251	I	189	229	252	2.59	255	377	484	82.19
		II	284	292	334	10.50	-	-	-	-
		III	394	400	491	20.15	-	-	-	-
		IV	617	715	735	27.24	-	-	-	-
		<i>Residue</i>				39.52				17.81
<b>Di5</b>	226	I	290	300	352	8.89	300	517	563	74.86
		II	352	373	423	8.74	-	-	-	-
		III	423	482	505	8.20	-	-	-	-
		IV	622	657	693	8.58	-	-	-	-
		V	693	755	771	12.15	-	-	-	-
		<i>Residue</i>				53.44				25.14
<b>Di7</b>	175	I	275	287	343	19.12	278	312	330	13.35
		II	428	473	499	15.14	372	419	517	67.38
		III	648	661	741	15.62	-	-	-	-
		IV	741	780	900	15.52				
		<i>Residue</i>				34.60				19.27

**Table 1.** Continued

<b>Di8</b>	228	I	292	307	357	22.08	302	326	385	13.90
		II	434	454	482	20.25	385	423	535	64.17
		III	629	638	672	8.32	-	-	-	-
		IV	720	740	900	7.17	-	-	-	-
		<i>Residue</i>				42.18				
<b>Di9</b>	168	I	165	175	208	8.56	162	179	203	12.14
		II	208	222	267	9.43	274	375	404	69.53
		III	267	281	311	7.49	-	-	-	-
		IV	404	450	518	11.79	-	-	-	-
		V	731	757	764	10.63				
		<i>Residue</i>				52.10				18.33

two parameters. After a few trial runs, the coefficient values were set at 5 and 2, respectively, because the initial temperature at which the degradation process starts is generally considered as the most important factor in determining the thermostability of a compound [21]. The obtained  $T_c$  values for the symmetrical derivatives analyzed in this work are presented in Fig. 3.

Considering the  $T_c$  temperature calculated *via* Eq. (1) as a measure of the thermal stability, the following stability series were established for the analyzed ferrocene derivatives:

$$\mathbf{Di2 < Di9 < Di1 < Di3 < Di7 < Di5 \cong Di8}$$

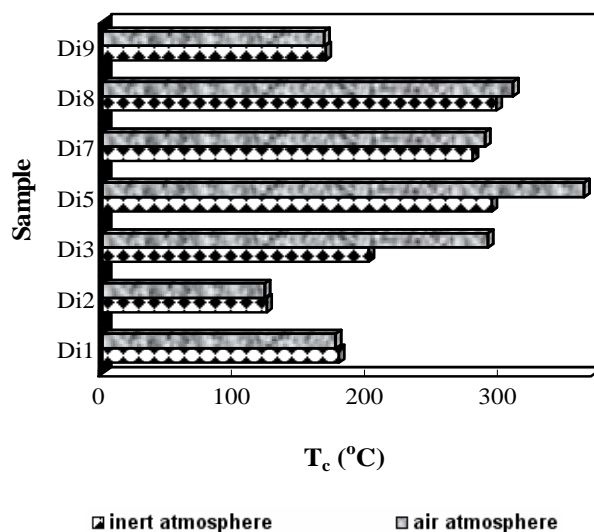
(in inert atmosphere of  $N_2$ )

$$\mathbf{Di2 < Di9 < Di1 < Di3 \cong Di7 < Di8 < Di5}$$

(in air)

The results show inversions in the thermostability order depending on the thermal degradation atmosphere in the case of **Di5** and **Di8** derivatives. The thermostability change as a function of the degradation atmosphere is related to the way in which the ester part is connected to the ferrocene and to the number of linking groups.

Table 1 shows the melting temperatures of the analyzed compounds, values that were gathered from the DTA curves.

**Fig. 3.** The values of the  $T_c$  parameter.

Further analysis of the results showed that the ferrocene derivatives, whose melting temperature was lower than their thermal decomposition temperature, enjoyed very good thermal stability ( $T_{onset} > 270$  °C), namely **Di5**, **Di7**, **Di8**. One possible explanation is that, in appreciating thermal degradation, not only a molecule should be considered, but also the neighboring molecules, so that the intermolecular

forces would assume a significant role. These forces determine the melting point of material and, in consequence, the aggregation state of the material at a certain temperature. According to the thermogram, regarding **Di1**, **Di2**, **Di3** and **Di9** derivatives, thermal degradation started before the observed melting point on the DTA curves, so that the material was in the solid state. In solid state, molecules were stacked together and only vibrations were possible. The crystalline network accumulated a large amount of energy and degradation started earlier in the case of **Di1**, **Di2**, **Di3** and **Di9** derivatives.

In order to gather additional data on the influence of the structure of the analyzed compounds on the thermal stability, we conducted conformational studies using the Dmol<sup>3</sup> module of the Materials Studio 4.0 software [22]. Figures 4 and 5 show the geometry of the investigated compounds, studied at

the lowest energy level.

The simulated properties of the symmetrical two-ferrocenyl derivatives, shown in Table 2, enabled us to reach the following conclusions concerning the molecular structure-thermal stability relation. The dipole moment values varied between 0.8 and 5.2. The resulting values were higher, over 1.5 Debye, for the symmetrical ferrocene derivatives with a central flexible core, where the initial degradation temperature ( $T_{\text{onset}}$ ) was higher than 270 °C. The only exception was the **Di9** compound, whose structure differed from that of the **Di8** derivative in the orientation of the ester group and whose dipole moment had low thermal stability, despite its high value (4 Debye). The high dipole moment values resulted in strong interactions between molecules, which led to higher thermal degradation temperature values. The analysis of the data gathered through molecular modeling also revealed that

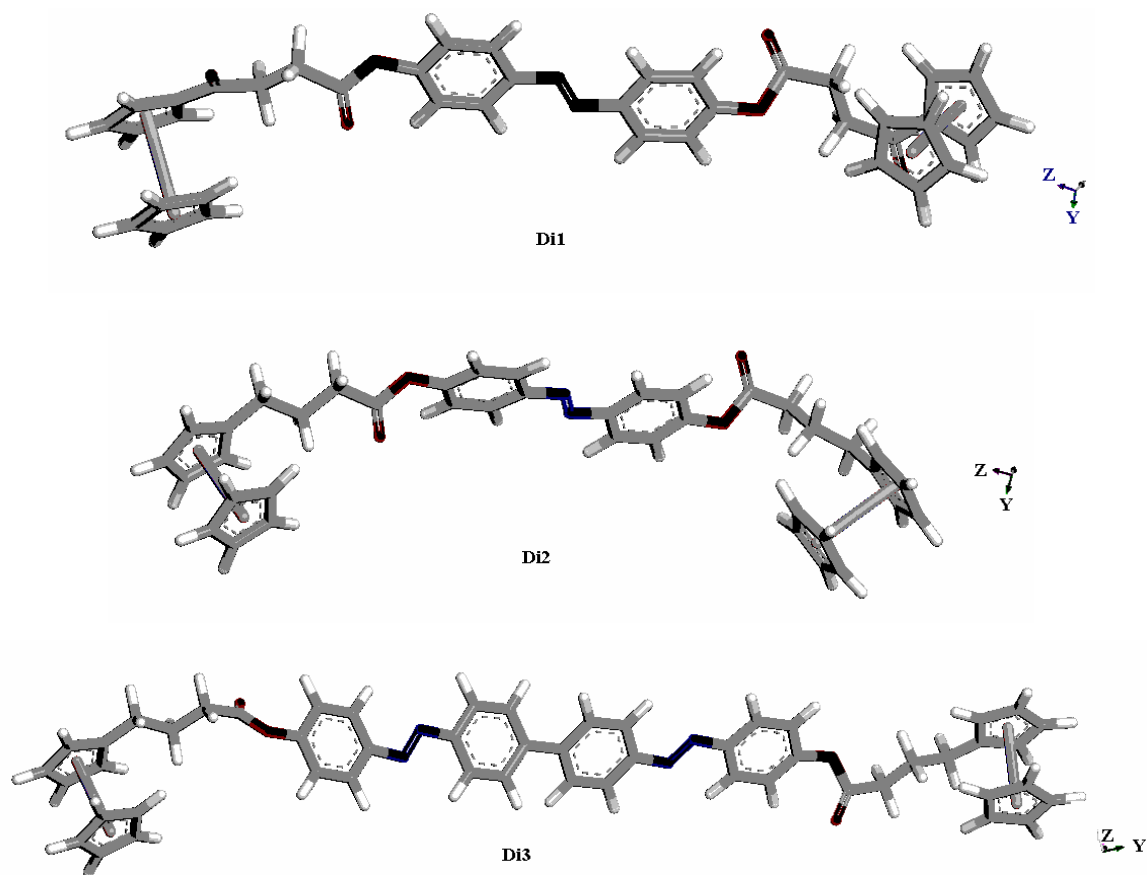
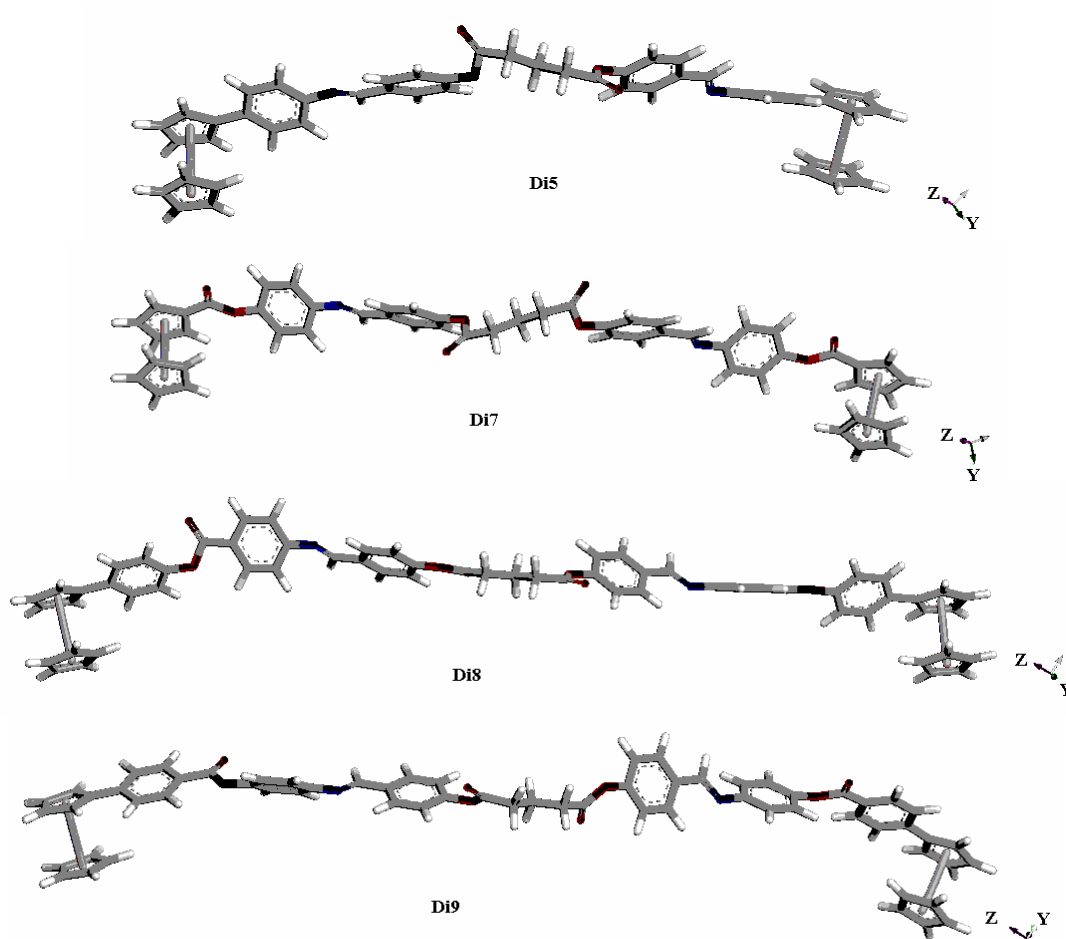


Fig. 4. The ferrocene derivatives (**Di1**, **Di2** and **Di3**) structure optimised by Dmol<sup>3</sup> module.



**Fig. 5.** The ferrocene derivatives (**Di5**, **Di7**, **Di8** and **Di9**) structure optimised by Dmol<sup>3</sup> module.

**Table 2.** Molecular Properties of the Symmetrical Derivatives with Two Ferrocenyl Units

Sample	Approx. surface (Å)	Volume (Å <sup>3</sup> )	Dipole moment (Debye)	Polarizability (Å <sup>3</sup> )	Molecular weight (uam)	Angle <sup>a</sup> (°)	Asymmetry factor <sup>b</sup> S = L/d
<b>Di1</b>	603.6	631.4	1.1	66.48	750.41	164.7	5.2
<b>Di2</b>	606.8	622.2	0.8	66.31	722.45	161.3	3.9
<b>Di3</b>	773.8	790.4	1.4	87.69	902.65	177.3	7.5
<b>Di5</b>	731.4	747.5	1.6	83.60	858.60	124.9	3.2
<b>Di7</b>	795.7	805.0	5.2	88.72	946.62	137.5	4.5
<b>Di8</b>	936.5	953.9	2.8	108.04	1098.81	147.7	5.0
<b>Di9</b>	934.4	956.4	4.0	108.04	1098.81	141.7	4.6

<sup>a</sup>Angle of the symmetry axes of the mesogenic groups. <sup>b</sup>Asymmetry factor calculated as ratio of total length/molecular diameter.

symmetrical ferrocene derivatives with a central flexible core, whose thermal stability was higher, had an angle between the molecular symmetry axes of their mesogenic components whose value was lower than 150 degrees, while the values of the asymmetry parameter, defined as the ratio between total length and molecule diameter, varied between 3 and 5.

Differences between the chemical structures made possible the evaluation of the influence of various factors upon the thermal stability, such as: the number of connecting groups, the number of benzene units and the position of the flexible part.

### Connecting Groups Influence

The ferrocene derivatives containing a keto group immediately adjacent to the ferrocenyl unit (**Di1**) showed a higher thermostability than the analogous derivatives in which the ketone functional group was reduced to the methylene one (**Di2**). Also, the symmetrical ferrocene derivative bearing an esteric group, with electron attracting effect (**Di7**), positioned immediately adjacent to the ferrocenyl units, showed lower thermostability than the derivative in which the ferrocenyl units were connected directly to an aromatic ring (**Di5**). This is probably a consequence of the fact that the group was in conjugation with the cyclopentadienyl moieties belonging to the ferrocene and induced a destabilization of the retroactive  $\pi$  bonds established between the iron atoms and the ferrocene resulting in lower thermal stability.

The esteric group orientation also influenced the thermostability, as it is evident from the  $T_c$  values obtained for samples **Di8** and **Di9**.

### The Influence of the Benzene Unit Number

By comparing the  $T_c$  parameter values obtained for samples **Di2** and **Di3**, that contain two and four benzene rings respectively, a significant thermostability increase was revealed, especially when the degradation was performed in air. This is mainly due to the presence of the 4,4'-bis(4-benzene-azo) diphenyl unit located in the center of the **Di3** molecule and, to a lesser extent, due to the increase of the benzene unit number from two to four. On the other hand, by comparing the ferrocene derivative containing six benzene rings, **Di9**, with the compound containing only four benzene moieties (**Di5**), an increase in the thermal stability by more

than 100 °C was revealed. This behavior is probably due to an increase in the number of linking groups that connect the benzene rings, leading to lower thermal stability and to facile elimination of small molecules such as  $N_2$ ,  $CO_2$ ,  $CO$  or  $CH_2O$  by breaking the azo, iminic or esteric bonds.

### The Influence of the Flexible Part Position

By comparing the characteristic temperatures shown by the derivatives containing a central flexible unit (**Di5**, **Di7**, **Di8**) with the ones shown by the derivatives that had marginal flexible moiety (**Di1**, **Di2**, **Di3**), a better thermal stability was in the cases in which the flexible part had a central position.

### The Influence of the Thermal Degradation Atmosphere

The degradation in air was more advanced and took place at a higher rate -the final temperature being mostly in the range of around 600 °C, while in nitrogen, the degradation rate was lower, the final temperature being at around more than 900 °C, although the residue percentage was more than 53%. The results can be easily explained considering the fact that the presence of oxygen in air favored the degradation and the thermo oxidation of the carbon residue, while in nitrogen; this residue was suppressed by the metal contained in the molecules. The differential thermal analysis results (Fig. 2c) suggest the occurrence of thermo oxidation in air.

## CONCLUSIONS

The thermal analysis characterization was evidence of a structure-thermostability relationship, demonstrating that the following factors affected the latter: the way the ester group is linked to the ferrocene, the number of linking groups, the number of benzene rings and the position of the flexible part. The effect of degradation atmosphere (air or nitrogen) upon the thermal stability was also observed. Our findings would facilitate the synthesis of new derivatives with certain thermal stability optimizing their industrial applications.

## ACKNOWLEDGEMENTS

This work was supported by CNCSIS-UEFISCSU, project number PNII-IDEI 600/2007.

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