

*Dedicated to the memory of
Professor Mircea D. Banciu (1941–2005)*

NEW THERMOTROPIC AZOMETHINES CONTAINING SULFONYL GROUP

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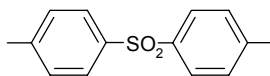
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The preparation, characterization and thermotropic properties of some low-molecular azomethines containing sulfonyl group, are described. The azomethine compounds contained besides azomethine units as calamitic mesogens, diphenyl sulfone units as nonmesogens. The effect of sulfonyl group on the mesomorphic behavior and molecular properties was estimated.

INTRODUCTION

Aromatic polyazomethines (PAMs) are an attractive class of high performance polymers, due to their potential applications such as information storage, nonlinear optics, laminates and films with good thermal stability. Unfortunately, PAMs are in general infusible polymers and have poor solubility, drawbacks which would minimize their practical applications.^{1,2} Various chemical modifications of their structures were used with the aim to reduce the melting temperature, to improve the solubility and to promote specific properties such as mesomorphism.³

Aromatic poly(ether sulfone)s (PES) are a family of aromatic amorphous thermoplastics with unique high – performance properties as engineering materials. Against the PAMs, PES have good solubility and low transition temperatures. A key structural feature of these polymers that distinguishes them from other aromatic polymers is the presence of the para-linked diarylsulfone group as part of the main backbone repeat unit:



The introduction of diarylsulfone group makes very effective kinks of the backbone and also has an important influence on the transition temperatures and solubility.⁴

Up to date there are few reported data describing the influence of sulfonyl group on the properties of low molecular weight azomethines.⁵ Keeping all these information in mind, we proposed to investigate the influence of the sulfonyl group on the thermal behavior and solubility of symmetrical low molecular weight azomethines. In this respect we synthesized six new azomethine compounds by the reaction of previously prepared and investigated mesogenic phenols⁶, with bis(*p*-chlorophenyl)sulfone.

RESULTS AND DISCUSSION

The structures of the phenolic intermediates used in this paper and their thermal behavior are enclosed in Table 1.

Table 1
Structures and thermal behavior of mesogenic phenols used

Mesogenic core	End group (R)	Transition temperatures (°C)
		Cr ^a 288 ^b I
	-NO ₂	Cr 165 ^b I
		Cr 226 ^b I
		Cr 225 ^c LC 237 I
	-NO ₂	Cr 242 ^c LC - ^d I
		Cr 272 ^c LC - ^d I

^a Cr = crystalline; LC = liquid crystalline; I = isotropic. ^b By optical polarized microscopy (OPM) measurements.
^c By DSC, 10 °C / min first heating scan, under nitrogen. ^d Could not be measured.

The synthetic pathway to azomethine sulfone compounds (**AMS**) was the classical Williamson etherification reaction, in which bis(*p*-chlorophenyl)sulfone reacted with mesogenic phenols as nucleophiles, in a 1:2 molar ratio (Scheme 1).

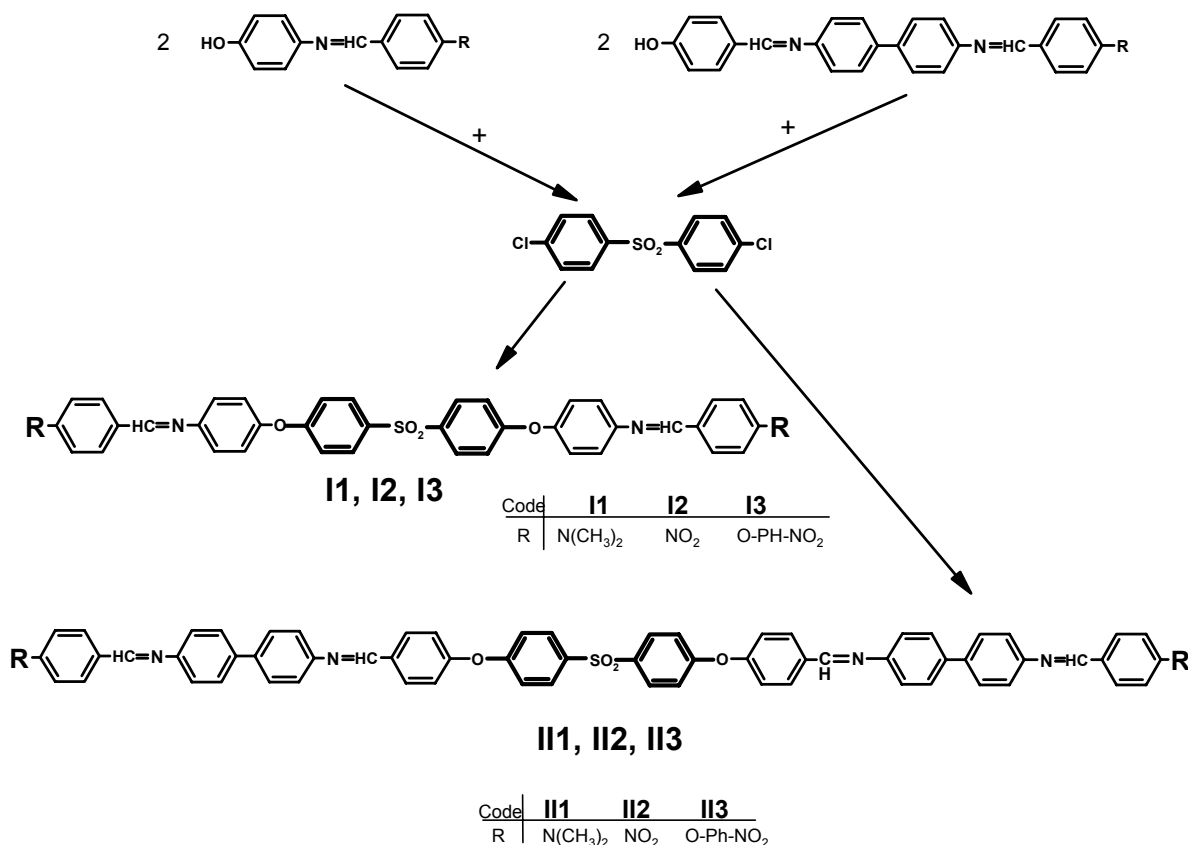
The expected structures of the synthesized **AMS** were confirmed by IR, ¹H-NMR spectroscopy and elemental analysis measurements. These results are presented in table 2.

The absence of any peaks in the region of 3500 cm⁻¹ (O-H) and 1097 cm⁻¹ (C-Cl) belonging to reaction partners, together with the appearance of intense absorption band at 1250 – 1260 cm⁻¹ (C-O-C, linkage created) suggested that the proposed structures are obtained. Also, the presence of specific azomethine (-CH=N-) absorption band at 1620 – 1635 cm⁻¹ and sulfonyl (SO₂) absorption bands (1330 cm⁻¹, assym. and 1160 cm⁻¹ sym.) confirmed the proposed structures (Table 2).

¹H-NMR spectra of the **AMS** showed the characteristic peak at 8.45 – 8.86 ppm assigned to the azomethine (CH=N) proton. Also, data in table 2 showed good agreement between the calculated and found values for nitrogen and sulphur of the **AMS** compounds.

UV spectra were recorded for all the compounds in DMF solutions. The data are collected in Table 2. All the samples exhibited an intense absorption band ranging between 319 nm and 380 nm, due to the π-π* electronic transition of the Ph-CH=N-Ph systems. Similar absorption maxima were reported for other azomethines.⁷ From the chemical structure point of view the compounds under investigation could be divided in two series: the first one I1 – I3 contains a mesogenic core with low length; the second one II1 – II3 contains a mesogenic core with higher length. It is expected that the series II to possess a more extended internal conjugation than the series I. This was really observed in the UV spectra (Table 2), i.e. in both series the λ_{max} decrease in order of the decreasing of conjugation (λ_{I3} < λ_{I2} < λ_{I1} and λ_{II3} < λ_{II2} < λ_{II1}).

The solubility of these compounds was tested in various organic solvents such as N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), N-methylpyrrolidine-2-one (NMP), N, N-dimethylacetamide (DMAA), tetrahydrofuran (THF), 1,4-dioxane, acetonitrile, acetic acid, acetone, chloroform, ethyl acetate, diethyl ether (Table 3). From table 3 one can see that, in dipolar aprotic solvents, the compounds from series **I**, containing lower length of the mesogenic core, have very good solubility, while the other ones have poorer solubility. In solvents like chloroform, methanol, acetone, ethyl acetate, diethyl ether, both series showed poor solubility, except for the compound **II**, which contains a small length of the mesogenic core and alkyl end groups.



Scheme 1 – Synthesis of azomethine sulfone compounds I1 – I3, II1 – II3.

Table 2

Spectral and elemental analysis data of the AMS I1 – I3, II1 – II3

AMS code	Molecular formula/ Formula weight	Elemental analysis		IR absorption bands due to the various stretching vibrations (cm ⁻¹)	λ ^a _{max} / nm
		N %	S %		
		calc. (found)			
I 1	C ₄₂ H ₃₈ N ₄ O ₄ S 694.86	8.06 (7.42)	4.61 (4.12)	3060 (ν=C-H aromatic), 2920, 2880, 2840 (νCH ₃), 1625 (νCH=N), 1590, 1490 (νC=C, aromatic), 1335 (νSO ₂ asym.) and 1160 (νSO ₂ sym.), 1255 (νC-O-C).	358
I 2	C ₃₈ H ₂₆ N ₄ O ₈ S 698.72	8.02 (7.70)	4.59 (4.23)	3075 (ν=C-H aromatic), 1630 (νCH=N), 1590, 1495 (νC=C, aromatic), 1520 (νNO ₂ asym.) and 1355 (νNO ₂ sym.), 1330 (νSO ₂ asym.) and 1160 (νSO ₂ sym.), 1250 (νC-O-C).	350
I 3	C ₅₀ H ₃₄ N ₄ O ₁₀ S 882.91	6.35 (6.86)	3.63 (3.41)	3075 (ν=C-H aromatic), 1635 (νCH=N), 1595, 1510 and 1500 (νC=C, aromatic), 1515 (νNO ₂ asym.) and 1355 (νNO ₂ sym.), 1340 (νSO ₂ asym.) and 1165 (νSO ₂ sym.), 1260 (νC-O-C).	319
II 1	C ₆₈ H ₅₆ N ₆ O ₄ S 1053.3	7.98 (8.24)	3.04 (3.31)	3090 (ν=C-H aromatic), 2950, 2910, 2880 (νCH ₃), 1620 (νCH=N), 1595, 1510 and 1500 (νC=C, aromatic), 1335 (νSO ₂ asym.) and 1170 (νSO ₂ sym.), 1250 (νC-O-C).	380
II 2	C ₆₄ H ₄₄ N ₆ O ₈ S 1057.16	7.85 (8.27)	3.03 (3.43)	3080 (ν=C-H aromatic), 1620 (νCH=N), 1595, 1510 and 1500 (νC=C, aromatic), 1530 (νNO ₂ asym.) and 1360 (νNO ₂ sym.), 1330 (νSO ₂ asym.) and 1170 (νSO ₂ sym.), 1250 (νC-O-C).	365
II 3	C ₇₆ H ₅₂ N ₆ O ₁₀ S 1241.36	6.77 (7.23)	2.58 (2.97)	3080 (ν=C-H aromatic), 1630 (νCH=N), 1585, 1505 and 1490 (νC=C, aromatic), 1515 (νNO ₂ asym.) and 1355 (νNO ₂ sym.), 1340 (νSO ₂ asym.) and 1170 (νSO ₂ sym.), 1260 (νC-O-C).	358

^a UV measurement of DMF solutions.

Table 3

Solubility characteristics of model compounds AMS

Solvent Code	DMSO	DMF	NMP	THF	DMAA	CHCl ₃	Dioxane	Acetone	Acetonitrile	Diethyl ether	Ethyl acetate
I1	+ ^a	+	+	+	+	+	+	±	±	±	+
I2	+	+	+	+	±	±	±	±	-	-	±
I3	+	+	+	±	+	±	±	±	-	-	±
II1	±	±	±	±	±	±	±	±	±	±	±
II2	±	±	±	±	±	±	±	±	±	±	±
II3	±	+	±	±	±	±	±	±	-	±	±

^a +: soluble; -: insoluble; ±: partially soluble.

Thermal behavior of the AMS compounds was observed by optical polarized microscopy (OPM), thermo-optical analysis (TOA) and thermogravimetric analysis (TGA). The data are enclosed in table 4.

Table 4

Thermal behavior of AMS

AMS code	OPM	TOA	TGA ^b	
			T ₀	T ₁₀
I1	Cr ^a 162 LC 178 I I 150 LC frozen	Cr 164 LC 180 I	225	388
I2	Cr 173 LC 187 I	Cr 202 LC 228 I ^c	120	412
I3	Cr 105 I	Cr 100 I	-	-
II1	Cr 250 LC ₁ 279 LC ₂ 292 I I 150 LC ₂ frozen	Cr 206 LC 248 I ^c	130	392
II2	Cr 197 LC - ^c I	-	208	300
II3	Cr 134 LC ₁ 187 LC ₂ 296 I I 288 LC ₂ frozen	Cr 138 LC ₁ 196 LC ₂ 292 I ^c	240	462

^a Cr = crystalline; LC = liquid crystalline I = isotropic;

^b Thermogravimetric analysis (TGA); T₀ = initial decomposition temperature; T₁₀ = temperature at which 10% weight loss occurred. ^c with decomposition.

Figure 1 shows representative plots of weight residue (wt. %) versus temperature, up to 600°C. The compounds exhibited good thermal stability: the decomposition started around 200°C, but 10% weight loss was recorded at temperatures around 400°C, except for the sample II 2 which had T₁₀ value at 300 °C.

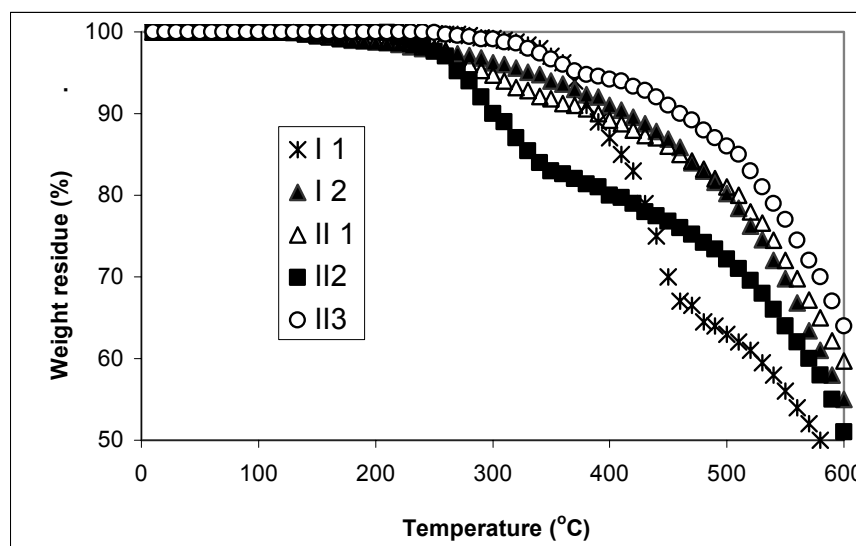


Fig. 1 – The thermal stability of the compounds evaluated by TGA in air.

A birefringent fluid observed under optical polarized microscopy (OPM) is the confirmation of liquid crystallinity⁸ and our OPM data revealed interesting thermal behavior for AMS compounds. The samples I1, I2, and series II showed a strong birefringence on heating. The observed textures are generally fine granulated (Figure 2a), similar to those reported for thermotropic polymers having stiff chains, without flexible spacers.⁹ The samples II1, II3 showed both fine granulated and schlieren textures¹⁰ (Figure 2b), which recovered under cooling and remained frozen. For samples I1, I2 and II2, no textures appeared on cooling, probably due to the partial decomposition of the samples near the clearing temperature. The compound I3 didn't show any birefringence in the melting state.

Some differences between the transition temperatures recorded by OPM versus TOA methods were observed. These differences could be explained by variations of the heating/cooling rate, amounts of sample used and sample preparation procedure used.¹¹

Representative thermograms obtained by TOA analysis of thermotropic compounds are given in figure 3.

As can be seen in figure 3 the T_m transitions on thermo-optical analysis (TOA) curves corresponded to a strong increase of the intensity of transmitted light, while the T_i transitions were evidenced as a slow decrease of the light intensity, because isotropization process is generally accompanied by flow of the texture.

The structural features of the mesogenic groups affect the onset, nature, and stability of the liquid-crystalline mesophases through their rigidity, their polarizability and their aspect ratio.¹²

When discussing the series I, we observed that sample I3, containing a mesogenic core with the smallest length (9.35 Å), comprised between two ether linkages, melted at 105 °C into an isotropic phase, without any intervening mesophase. In case of sample I1, the addition of a dimethylamino end group, instead of p-nitro phenoxy group, led to an increase of mesogenic core's length to 10.16 Å, due to the involvement of nitrogen atom into extended conjugation.

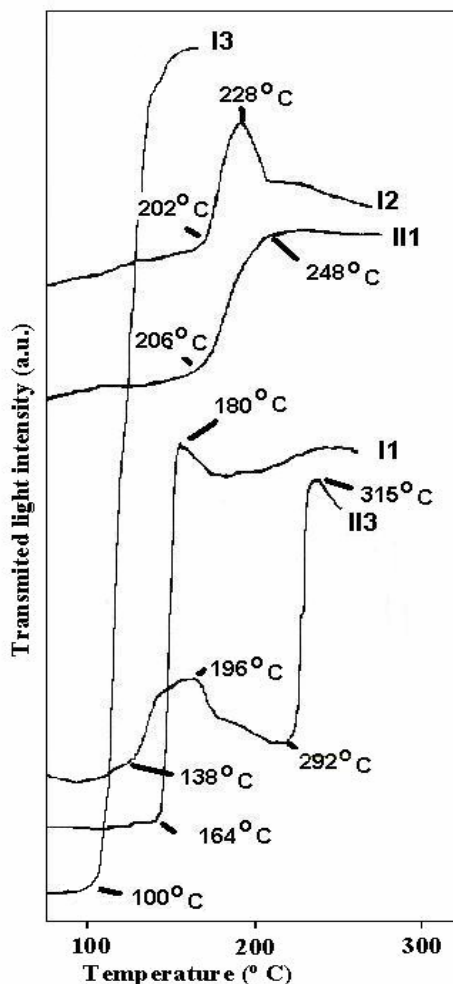


Fig. 3 – TOA curves for I1 – I3, II1, II3 samples.

This fact had as consequence the increase of melting transition up to 162 °C and the appearance of a liquid crystalline phase, which maintained for a further 16 °C above the melting point. A much more increase of the mesogenic core's length was realized in case of sample I2 (10.79 Å) by coupling a *p*-nitro group instead of *p*-dimethylamino group. As consequence, the melting transition increased at 173 °C.

For series II we observed a similar behavior. The compound II3 which contain the mesogenic core between two ether linkages had the lowest melting point and the largest mesophase stability of this series. The II1 and II2 compounds having N(CH₃)₂ and NO₂ end groups respectively, presented mesophases, at higher temperatures.

As can be seen, the incorporation of end groups which increase the length of the mesogenic core increase the melting transition.

The geometrical features of the **AMS** compounds were exemplified on an azomethine-ether-sulfone fragment, by using molecular modelling method (MM+) ¹³. We observed that rotations around the ether bonds minimize the disruptive influence of the kinked units on the straightness of the chain.

CONCLUSIONS

New azomethine compounds, derived from azomethine phenolic intermediates and bis(*p*-chlorophenyl)sulfone were prepared in order to obtain more information about the properties of azomethines containing diphenylsulfone as kinking group.

All the compounds have good thermal stability and insignificant weight loss until 370 °C. The azomethinic compounds present good solubility in common organic solvents.

Although the diphenylsulfone moiety is unfavourable for liquid crystalline behaviour, thermotropic properties occurred when such unit was incorporated into the structures of AMS compounds. The creation of the mesophase was possible by using a kinking unit instead of a spacer between mesogenic units. The melting and isotropization transition temperatures were accessible and strongly decreased when the mesogenic core was linked supplementary by two ether linkages.

The incorporation of diphenylsulfone moiety by means of ether linkages into the structure was useful for improving the solubility and for decreasing the melting and the isotropization temperatures.

EXPERIMENTAL

Reagents

Bis(4-chlorophenyl)sulfone from Fluka was recrystallized from toluene (mp 148 – 149 °C). Dimethylsulfoxide (DMSO) was dried over calcium hydride and distilled under vacuum before use. Anhydrous potassium carbonate was dried at 120 °C in a vacuum oven before use.

Measurements

Infrared (IR) spectra were recorded on a Specord M80 Carl Zeiss Jena Spectrophotometer, using KBr pellets. Proton nuclear magnetic resonance (¹H-NMR) spectra were recorded by a Jeol 60 MHz spectrometer using DMSO-d₆ as solvent and tetramethylsilane (TMS) as internal reference. Chemical shifts are reported in parts per million (ppm). UV spectra were obtained on Carl Zeiss Jena SPECORD M42 spectrophotometer in DMF solutions using 10 – mm quartz cells fitted with poly(tetrafluoroethylene) stoppers. Mesophases for thermotropic compounds have been studied by observation of the textures with an Olympus BH-2 polarized light microscope under cross polarizers, fitted with a THMS 600/HSF91 hot stage. The temperature at which isotropic phase occurred was taken as the isotropization temperature (T_i). Thermo-optical analysis (TOA) was carried out with a homemade apparatus. ¹⁴ Thermogravimetric analysis (TGA) was carried out by using a MOM Q Derivatograph, Hungary, at a heating rate of 9°C/min, in air. Solubility tests of the compounds were performed in various common organic solvents such as: acetone, methanol, carbontetrachloride, chloroform, acetonitrile, dimethylsulfoxide, N,N-dimethylformamide (DMF), N-methylpyrrolidine-2-one (NMP).

Synthesis of the AMS

The preparation of the azomethine phenolic intermediates was performed by acid-catalyzed condensation reaction. Synthesis and characterization of the phenols used in this study were previously reported. ¹²

The synthetic pathway to azomethinic sulfone compounds was the classical Williamson etherification reaction, in which bis(*p*-chlorophenyl)sulfone reacted with a mesogenic phenol as nucleophile, in a 1:2 molar ratio (Scheme 1). A typical procedure is as follows: 0.42 g (1.457 mmol) of bis(*p*-chlorophenyl)sulfone, 0.7 g (2.913 mmol) of *p*-[*p*-(N,N-dimethylamino)benzylideneimino]

phenol, 0.28 g anhydrous potassium carbonate (15 % molar excess) and 8 mL DMSO were charged into a round bottom flask fitted with thermometer, condenser, nitrogen inlet and magnetic stirrer. The temperature was gradually increased to 100 °C during one hour. Then the temperature was quickly increased to 160 °C and the reaction mixture was maintained under stirring for 6 h. After cooling, the brown reaction mixture was poured into water and the solid compound **11** was filtered, washed with water and then extracted in a Soxhlet with methanol for 5 h. Finally, the compound was vacuum dried at 60°C for 18 h. Similar procedures were used to prepare and purify the other **AMS** compounds.

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