SYNTHESIS AND CHARACTERIZATION OF NEW DIAMINES CONTAINING SIDE SUBSTITUTED AZOBENZENE GROUPS

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New aromatic diamines containing two side substituted azobenzene groups have been obtained by chemical modification of 2,2-bis(3-amino-4-hydroxyphenyl)–hexafluoropropane with different *p*-bromoalkyloxy-*p'*-methyl-azobenzene compounds in the presence of K_2CO_3/KI. The bromoalkyloxy-methylazobenzenes have been prepared by the reaction of *p*-hydroxy-*p'*-methyl-azobenzene with different dibromoalkanes. All intermediates and the prepared diamines have been characterized by melting points, infrared spectroscopy and proton nuclear magnetic resonance. The new diamines can be used further as monomers for production of new polyimides or copolyimides for high performance applications.
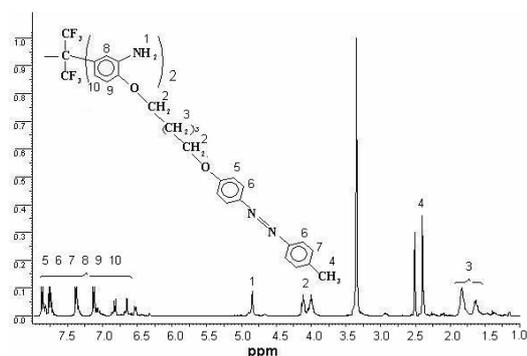
INTRODUCTION

The intense development of the domain of science and technology such as photonic and optoelectronic forces search of new materials. Due to their practical and potential applications, polymeric materials with nonlinear optical properties especially those containing azobenzene groups have attracted the interest of many groups of researchers in both fundamental and applied research area. These polymers show a fast optical response time, high laser damage threshold, and good mechanical and dimensional stability and can give the possibility of chemical modification.[1-7] Due to these advantages, some azopolymers have

been extensively investigated for photonic devices such as frequency modulators, optical switches, optical storage data, optical fibers.[8,9] The applications of azopolymers are based on reversible *trans-cis-trans* photoisomerization of the azobenzene group under irradiation with a linearly polarized light which lead to generation of photoinduced optical anisotropy in the material.[1, 10-12] Between the polymers which play a key role as materials for many various applications, aromatic polyimides were investigated as potential material in the field of photonics and optoelectronics, due to their excellent physico-chemical properties such as optical and thermal stability in combination with high glass transition temperature.[13-15] However,

one of the problems of polyimides is their poor solubility in organic solvents, which is an important drawback of processing the polymers into thin films. The incorporation of flexible links, methyl substituents or pendant groups has been sometimes found to increase the solubility.[16,17] The synthesis of polyimides which contain side azobenzene units implies the uses of monomers which incorporate these groups. The introduction of chromophore into a polyimide backbone enhances the chromophore's thermostability and improves the solubility.[15,17] Thus, synthesis of soluble, processable and thermally stable new azopolymers is highly desirable for the photonic technology. Azobenzene chromophores can be incorporated into polymer structure by direct polycondensation of the chromophore containing monomers or by post-Mitsunobu condensation between hydroxy-polyimides and hydroxy chromophores.[3, 18] Hence in order to obtain new materials it is necessary to synthesize new monomers and, the corresponding macromolecular compounds with special properties. Based on our previous experience in the synthesis of diamines with side azobenzene units and different azo-polymers (especially azo-polyimides)[19-26] in this paper is presented the synthesis of new monomers. These monomers are of special structure because contain two side substituted azobenzene groups in a single molecule of diamine and they are expected to lead to polymers or co-polymers with new and interesting properties. These monomers containing chromophores have been obtained by modification reaction of 2,2-bis(3-amino-4-hydroxyphenyl)–hexafluoropropane with different *p*-bromoalky-loxy-*p*'-methyl-azobenzenes in the presence of K_2CO_3/KI and were characterized by infrared and ^{1}H-NMR spectroscopy.

RESULTS AND DISCUSSION

The synthesis of the diamines namely 2,2 bis-(3-amino-4-oxypropyloxy-phenyl-4'-methylazobenzene) hexafluoropropane, 2,2 bis-(3-amino-4-oxybutyloxy-phenyl-4'-methylazobenzene) hexafluoropropane, 2,2 bis-(3-amino-4-oxypentyloxy-phenyl-4'-methy-lazobenzene) hexafluoropropane and 2,2 bis-(3-amino-4-oxyhexyloxy-phenyl-4'-methylazobenzene) hexafluoropropane was performed by Williamson reaction of 2,2-bis(3-amino-4-hydroxyphenyl)–hexafluoropropane with *p*-(bromalkyloxy)-*p*'-methyl-azobenzenes, compounds which contains preformed azobenzene groups. These intermediates

containing substituted azobenzene groups were synthesized by the reaction of diazotized *p*-toluidine with phenol, followed by the reaction with different dibromoalkanes. Herein are presented the reactions which lead to 2,2 bis-(3-amino-4-oxyalkyloxy-phenyl-4'-methylazobenzene) hexafluoropropane.

Synthesis of the azo-intermediate compounds

Synthesis of p-hydroxy-p'-methyl-azobenzene

This intermediate compound was obtained by a reaction which takes place in two steps at low temperatures (0-5°C) and pH 5-8 as previously reported for similar compound.[20] First step consist in diazotization of *p*-toluidine followed by the coupling of the formed diazonium salt with phenol (Scheme 1). 35 mL of concentrated hydrochloric acid and 35 mL water were added to 21.4 g (0.2 mol) of *p*-toluidine (*p*-methylaniline) and the resulting solution was cooled down to 0°C. Then a solution of 15 g (0.2 mol) of sodium nitrite in 30 mL water was added drop-wise and the mixture was stirred at a temperature between 0 and 5°C for 15 min. Second step, the resulting clear solution of diazonium salt was slowly added to a solution of 28.2 g (0.3 mol) phenol, 12 g (0.3 mol) NaOH, 32 g (0.3 mol) Na_2CO_3 in 150 ml water at 0-5°C. Sometimes it was necessary to add extra NaOH to avoid formation of foam. After complete addition, the mixture was stirred for 1–2 h at 0-5°C. The yellow-orange colored precipitate was filtered off, washed with water and then dried in a vacuum oven at 100°C. Melting point: 149-152°C. Yield: 96%.
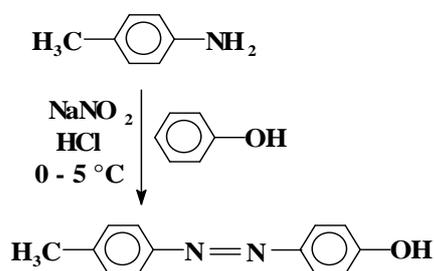
Scheme 1 – The synthesis of *p*-hydroxy-*p*'-methyl-azobenzene.

The FTIR spectrum of this intermediate compound (Fig. 1) shows the characteristic absorption peaks of methyl groups at 2920 cm^{-1} and the characteristic absorption bands of azobenzene which overlaps on those of benzene rings at 1600 cm^{-1}.
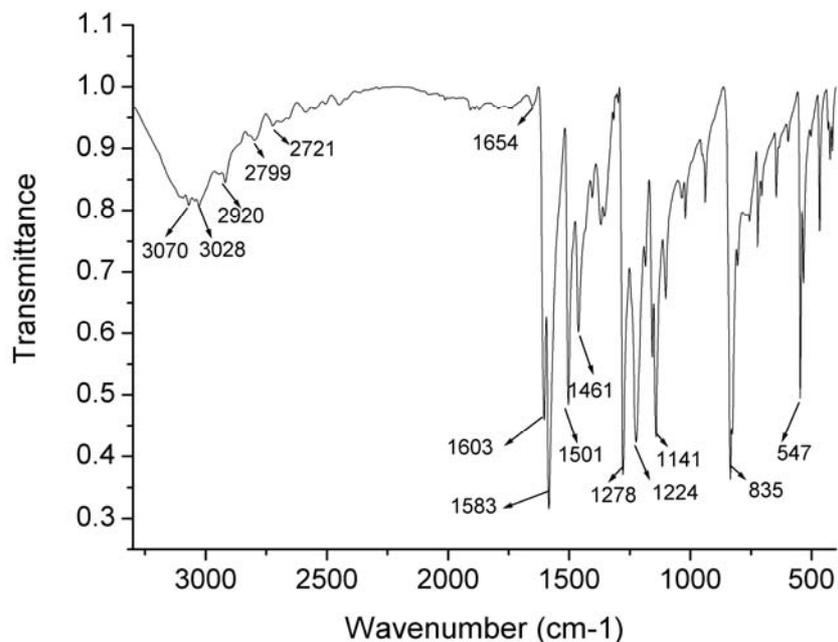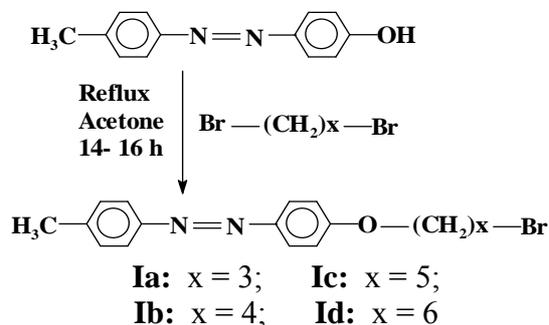
Fig. 1 – FTIR spectrum of *p*-hydroxy-*p'*-methyl-azobenzene.
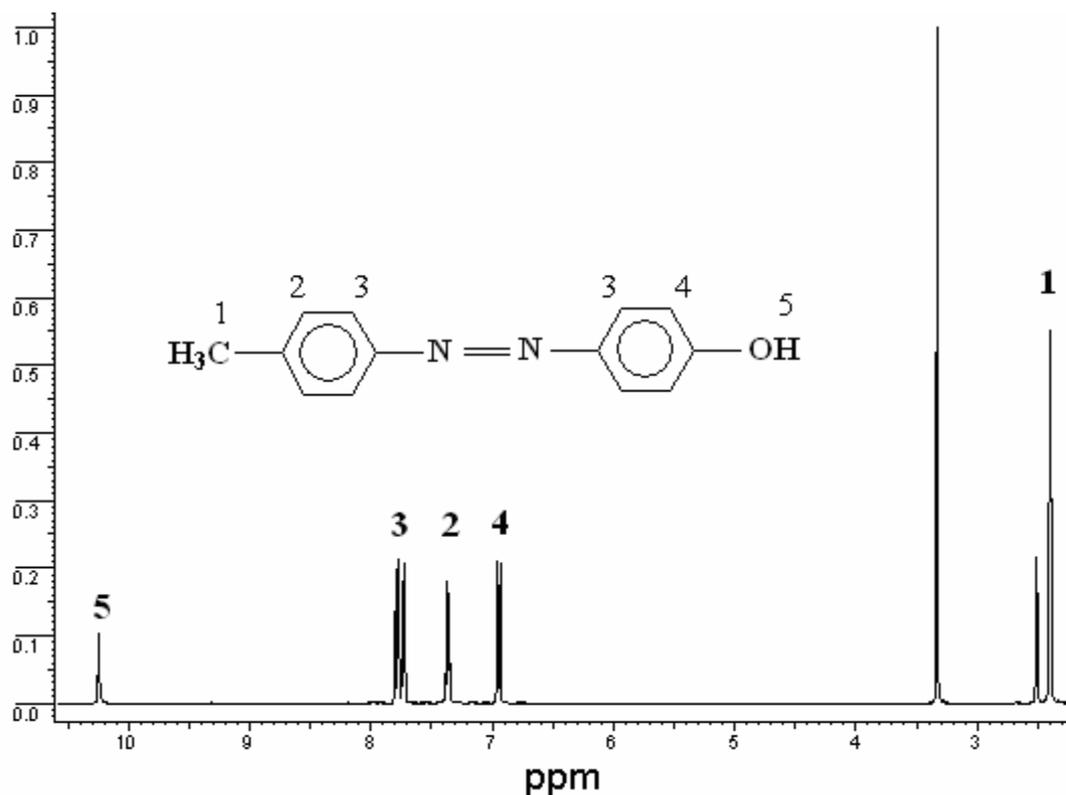
Fig. 2 – H^1-NMR spectrum of *p*-hydroxy-*p'*-methylazobenzene.

H^1-NMR (DMSO-d$_6$,) of *p*-hydroxy-*p'*-methyl-azobenzene (Fig. 2): 2.4 ppm aliphatic protons (s, 3H, CH$_3$); 7.35 ppm aromatic proton *ortho* to CH$_3$ (d, 2H); 7.77-7.79 ppm aromatic protons *orho* to -N=N- (d, 4H); 6.93 ppm aromatic protons *ortho* to OH (d, 2H) and 10.24 ppm proton of OH (s, 1H).

Synthesis of
p-(bromoalkyloxy)-*p'*-methyl-azobenzenes

These products have been obtained by the reaction of *p*-hydroxy-*p'*-methyl-azobenzene (above synthesized) with dibromoalkane by a procedure described in the literature.[21] The reaction

takes place at reflux temperature in acetone and the dibromo-compounds were taken in great excess (6÷10:1) (Scheme 2).

$$H_3C—◯—N=N—◯—OH$$

$$\text{Reflux} \atop \text{Acetone} \atop \text{14- 16 h} \Big| \quad Br—(CH_2)x—Br$$

↓

$$H_3C—◯—N=N—◯—O—(CH_2)x—Br$$

Ia: x = 3;   **Ic:** x = 5;
Ib: x = 4;   **Id:** x = 6

Scheme 2 – The synthesis
of *p*-bromoalkyloxy-methyl-azobenzenes.

A general procedure is given for one of these compounds, namely *p*-(bromopropyloxy)-*p'*-methyl-azobenzene, **Ia.**

Thus, a mixture of 60.6 g (0.30 mol) of 1,3-dibromopropane, 21 g (0.15 mol) K_2CO_3, 6.36 g (0.030 mol) *p*-hydroxy-*p'*-methyl-azobenzene and a trace of KI in 125 mL acetone was stirred vigorously and refluxed for 14 h (controlled by thin-layer chromatography). After cooling, the precipitated salt was filtered off and the filtrate was evaporated. The separated product was washed with ethanol and then it was dried in a vacuum oven at 60°C. Melting point: 109-110°C. Yield: 75%.

The same procedure was used for the synthesis of *p-(*bromobutyloxy)-*p'*-methyl-azobenzene;

p-(bromopentyloxy)-*p'*-methyl-azobenzene and *p*-(bromohexyloxy)-*p'*-methyl-azobenzene.

The FTIR spectrum of *p*-(bromopropyloxy)-*p'*-methyl-azobenzene (Fig. 3) showed the increasing of the characteristic absorption band in the region 2854 cm^{-1} and 2923 cm^{-1} for methyl and methylene units. The characteristic absorption bands of azobenzene which overlap on benzene rings at 1600 cm^{-1} and the presence of ether linkage at 1241 cm^{-1} were also evidenced.

The structures of these intermediates have been evidenced by H^1-NMR spectra (in DMSO-d_6 or $CDCl_3$) and the obtained results are shown below and they correspond to the synthesized compounds.

H^1-NMR (DMSO-d_6,) of *p*-(bromopropyloxy)-*p'*-methyl-azobenzene, **Ia** (Fig. 4): 2.40 ppm aliphatic protons (s, 3H, CH_3); 7.37-7.39 ppm aromatic proton *ortho* to CH_3 (d, 2H); 7.75-7.89 ppm aromatic protons *ortho* to -N=N- (d, 4H); 7.14-7.16 ppm aromatic protons *ortho* to O (d, 2H) 4.20 ppm aliphatic protons linked to O; 3.70 ppm methylene protons (d, 2 H) and 2.30 ppm methylene protons to Br (d, 2H).

H^1-NMR ($CDCl_3$) of *p*-(bromobutyloxy)-*p'*-methyl-azobenzene, **Ib:** 2.48 ppm aliphatic protons (s, 3H, CH_3); 7.36-7.40 ppm aromatic proton *ortho* to CH_3 (d, 2H); 7.83-7.96 ppm aromatic protons *ortho* to -N=N- (d, 4H); 7.03-7.05 ppm aromatic protons *ortho* to O (d, 2H) 4.13 ppm aliphatic protons linked to O; 3.56 ppm methylene protons to Br (d, 2 H) and 2.02-2.17 ppm methylene protons (d, 4H).
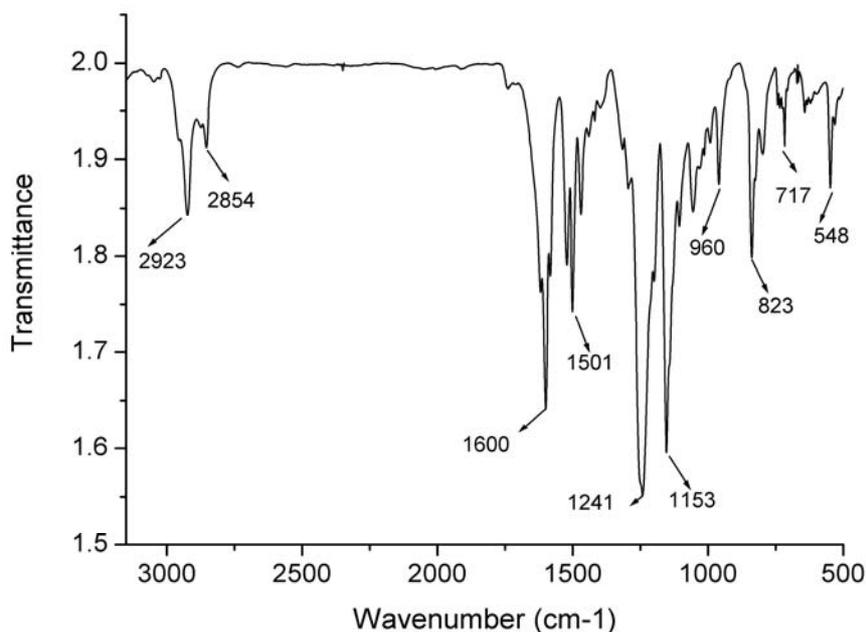

Fig. 3 – FTIR spectrum *of p*-(bromopropyloxy*)-p'*-methyl-azobenzene, **Ia.**
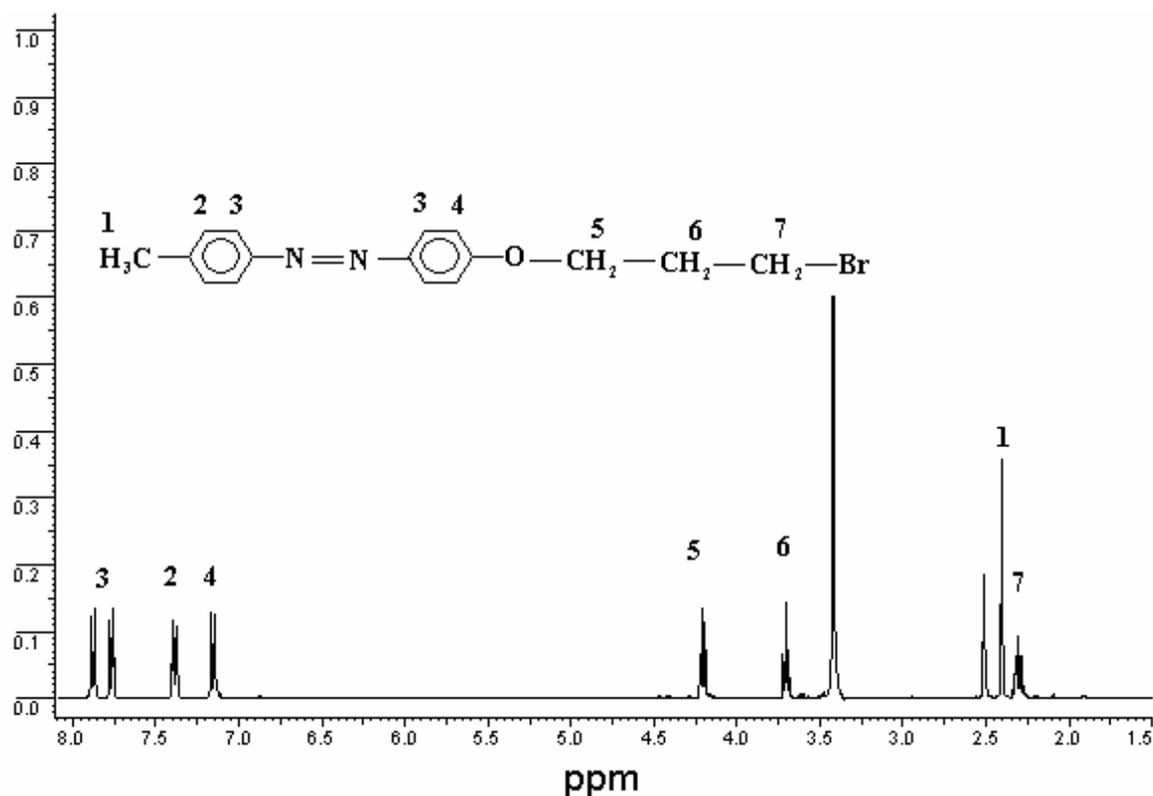
Fig. 4 – H^1-NMR spectrum of *p*-(bromopropyloxy)-*p'*-methyl-azobenzene, **Ia.**

Table 1

Preparation of *p*-(bromoalkyloxy)-*p'*-methylazobenzene (**Ia-d**)

Com-pound	*p*-hydroxy –*p'*-methyl azobenzene g / mol	Dibromo-compound g / mol	Acetone mL	K_2CO_3 / KI g	Time, h	Melting point °C	Yield %
Ia	6.36 / 0.03	60.6 / 0.3	125	21 / 0.05	14	109-110	75
Ib	6.36 / 0.03	64.8 / 0.3	110	21 / 0.05	15	90-91	70
Ic	6.36 / 0.03	69 / 0.3	110	21 / 0.05	14	109-112	74
Id	5.3 / 0.025	36.6 / 0.15	80	17.5 / 0.04	16	102-104	72

H^1-NMR (CDCl$_3$) of *p*-(bromopentyloxy)-*p'*-methyl-azobenzene, **Ic:** 2.48 ppm aliphatic protons (s, 3H, CH$_3$); 7.33-7.35 ppm aromatic proton *ortho* to CH$_3$ (d, 2H); 7.83-7.96 ppm aromatic protons *ortho* to -N=N- (d, 4H); 7.03-7.06 ppm aromatic protons *ortho* to O (d, 2H) 4.10-4.14 ppm aliphatic protons linked to O; 3.47-3.52 ppm methylene protons to Br (d, 2 H) and 1.72-2.05 ppm mthylene protons (d, 6H).

H^1-NMR (CDCl$_3$) of *p*-(bromohexyloxy)-*p'*-methyl-azobenzene, **Id:** 2.43 ppm aliphatic protons (s, 3H, CH$_3$); 7.28-7.30 ppm aromatic proton *ortho* to CH$_3$ (d, 2H); 7.78-7.91 ppm aromatic protons *ortho* to -N=N- (d, 4H); 6.98-7.00 ppm aromatic protons *ortho* to O (d, 2H) 4.05 ppm aliphatic protons linked to O; 3.436 ppm methylene protons to Br (d, 2 H) and 1.51-1.93 ppm methylene protons (d, 8H).

Details of the synthesis of the *p*-(bromoalky-loxy)-*p'*-methylazobenzenes (**Ia-d**) are shown in Table 1.

Synthesis of
2,2-bis{3-amino-4-[(p-oxyalkyloxy–p'-methyl)
azobenzene]-phenylene}-hexafluoropropane,
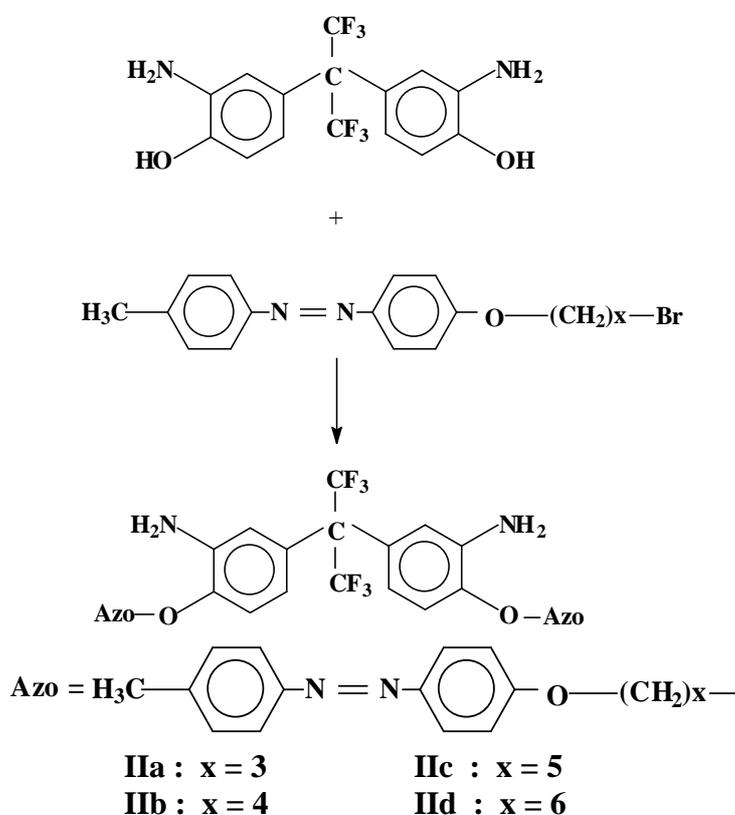### II a-d

The Williamson reaction has been used for obtaining of the diamines by using of an *ortho*-hydroxy diamine such as 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane and different alkyl halide such as *p*-bromoalkyloxy-*p'*-methyl-azobenzene)s. The reaction takes place at reflux, in acetone in the presence of K$_2$CO$_3$ and some traces of KI, for around 60 h (Scheme 3).

The general procedure is given for 2,2-bis{3-amino-4-[(*p*-oxyhexyloxy–*p*'-methyl) azobenzene]-phenylene}-hexafluoropropane, **IId**.

A mixture of 2.196 g (0.006 mol) of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane, 4.5 g (0.012 mol) of *p*-(6-bromobutane-oxy)-*p*'-methyl-azobenzene, 8.38 g (0.06 mol) K_2CO_3 and a trace of KI in 175 ml acetone was stirred vigorously and refluxed for 64 h. The necessary reaction time was determined by thin layer chromatography. After cooling, the precipitated salt was filtered off and the filtrate was concentrated by evaporation. The resulting compound was put into water, washed with water many times and then dried in a vacuum oven at 40°C. Yield: 93.5%. Table 2 shows the synthesis of azo-diamines. The same procedure was used for the synthesis of the others diamines, **II.**

The structure of the synthesized azo-diamines was identified by FTIR and H^1-NMR spectra. The FTIR spectrum of the synthesized 2,2-bis{3-amino-4-[(*p*-oxypenthyloxy–*p*'-methyl) azobenzene]-phenylene}-hexafluoropropane (Fig. 5) showed the characteristic absorption bands of amine group at 3450 and 3386 cm^{-1} and of methylene groups at 2940 cm^{-1} and 2870 cm^{-1}. The azobenzene group is overlapping on benzene rings at 1600 cm^{-1} and the ether bridge is present at 1244 cm^{-1}.

Scheme 3 – Synthesis of diamines containing two side substituted azobenzene groups **IIa-d**.

Table 2

Preparation of 2,2-bis{3-amino-4-[(*p*-oxyalkyloxy–*p*'-methyl) azobenzene]-phenylene}-hexafluoropropane, **IIa-d**

Azo-diamine	2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane g / mol	Bromoalkyl-oxy-compound g / mol	Acetone mL	K_2CO_3 / KI g	Time, h	Yield %
IIa	2.196 / 0.006	3.99 / 0.012	125	8.38 / 0.05	52	90
IIb	2.196 / 0.006	4.16 / 0.012	110	8.38 / 0.05	60	83
IIc	2.196 / 0.006	4.33 / 0.012	175	8.38 / 0.05	64	97
IId	2.196 / 0.006	4.5 / 0.012	175	8.38 / 0.04	64	93.5

H^1-NMR (DMSO-d$_6$) of 2,2-bis{3-amino-4-[(*p*-oxypropyloxy–*p'*-methyl) azobenzene]-phenylene}-hexafluoropropane: 2.40 ppm aliphatic protons (s, 6H, CH$_3$); 6.51-7.75 ppm aromatic protons (m, 22H); 4.94 ppm amine protons (d, 4H); 4.13-4.33 ppm aliphatic protons linked to O (d, 8H); 2.22-2.25 ppm methylene protons (d, 4 H).

H^1-NMR (DMSO-d$_6$) of 2,2-bis{3-amino-4-[(*p*-oxybutyloxy–*p'*-methyl) azobenzene]-phenylene}-hexafluoropropane: 2.40 ppm aliphatic protons (s, 6H, CH$_3$); 7.52-7.81 ppm aromatic protons (m, 22H); 4.87 ppm amine protons (d, 4H); 3.98-4.18 ppm aliphatic protons linked to O (d, 8H); 1.95 ppm methylene protons (d, 8 H).
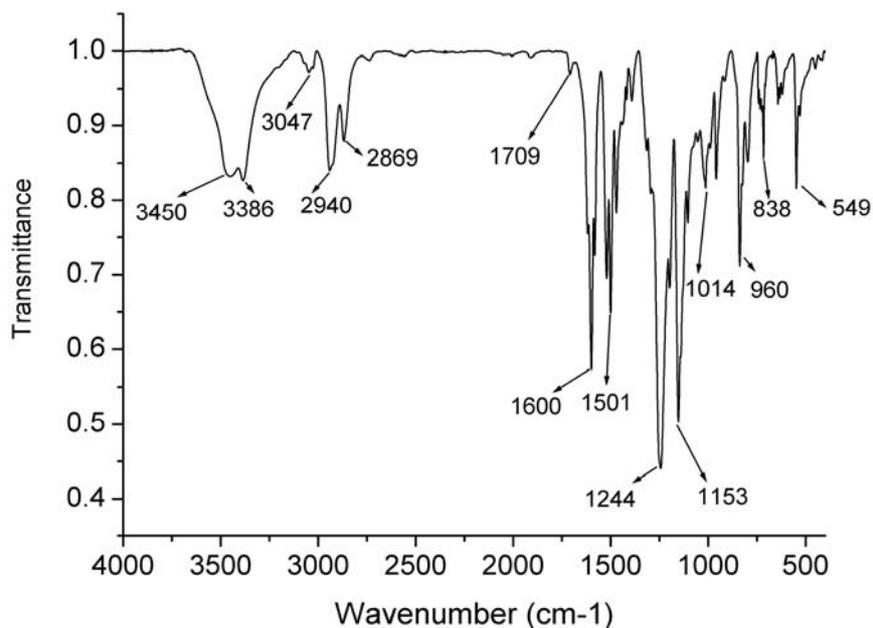

Fig. 5 – FTIR spectrum *of* 2,2-bis{3-amino-4-[(*p*-oxypenthyloxy–*p'*-methyl) azobenzene]-phenylene}-hexafluoropropane.
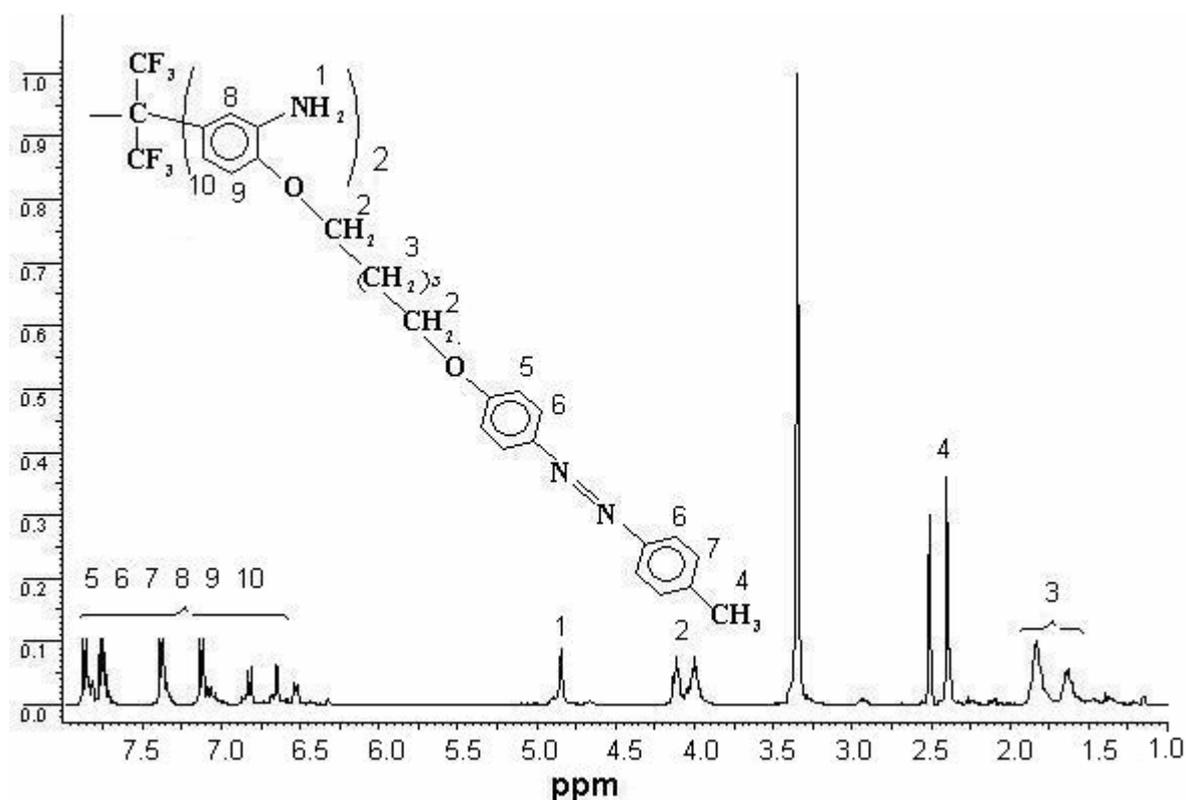

Fig. 6 – H^1-NMR spectrum of 2,2-bis{3-amino-4-[(*p*-oxypenthyloxy–*p'*-methyl) azobenzene]-phenylene}-hexafluoropropane.

H[1]-NMR (DMSO-d$_6$) of 2,2-bis{3-amino-4-[(*p*-oxypenthyloxy–*p'*-methyl) azobenzene]-phenylene}-hexafluoropropane (Fig. 6): 2.40 ppm aliphatic protons (s, 6H, CH$_3$); 6.51-7.77 ppm aromatic protons (m, 22H); 4.85 ppm amine protons (d, 4H); 3.98-4.13 ppm aliphatic protons linked to O (d, 8H); 1.59-1.84 ppm methylene protons (d, 12H).

H[1]-NMR (DMSO-d$_6$) of 2,2-bis{3-amino-4-[(*p*-oxyhexyloxy–*p'*-methyl) azobenzene]-phenylene}-hexafluoropropane}*:* 2.40 ppm aliphatic protons (s, 6H, CH$_3$); 6.30-7.82 ppm aromatic protons (m, 22H); 4.84 ppm amine protons (d, 4H); 3.93-4.11 ppm aliphatic protons linked to O (d, 8H) ; 1.52-1.79 ppm methylene protons (d, 16 H).

These azo-diamines are potential candidates for the synthesis of new compounds, especially polyimides or co-polyimides which can present new and interesting properties.

EXPERIMENTAL

Materials

p-Toluidine (97%), phenol (99%), 1,3-dibromopropane 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane (96%), NaNO$_2$ (99,9%), K$_2$CO$_3$ (anhydrous), KI (purris), acetone (p.a) were provided from different commercial sources (Sigma-Aldrich, Lancaster etc.) and were used as received.

Measurements

FTIR spectra were recorded with a FTS 3000 MX Exalibur spectrometer (Digilab/Bio-Rad, Thermo Scientific Company, USA), in atenuate reflexion mode (ATR). ^{1}H-NMR spectrum was recorded using a spectrometer Bruker Avance DRX 400 in DMSO-d$_6$ or CDCl$_3$ with TMS as internal reference.

CONCLUSIONS

New diamines which contain two side substituted azobenzene groups have been obtained by using Williamson reaction of 2,2-bis(3-amino-4-hydroxyphenyl) hexafluoropropane with bromoalkyl-oxy-4'-methyl-azobenzenes. The structure of these diamines was evidenced by FTIR and ^{1}H-NMR spectrometry. The obtained diamines can be used in the synthesis of polymers or copolymers with new and interesting properties.

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