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New aspects on the synthesis and properties of some azoxy- and azo-group containing compounds

E. SCORTANU*, C. PRISACARIU
The Romanian Academy's Institute of Macromolecular Chemistry "Petru Poni",Iasi, 700487, Romania

The paper deals with a new method of preparation of azobenzene containing compounds consisting in small molecules or polymers, by a reductive coupling reaction of some nitrobenzene derivatives: p- or o-nitrotoluene, 4,6-dinitro-1,3-xylene or 4,4'-, 2,4', 2,2'-dinitro-dibenzyl. The reductive coupling reaction was achieved starting to nitro derivative and natrium hydroxide into methanol when azoxy- or/and azo group containing products were obtained. All products were characterized by IR and UV spectra, solubility, thermogravimetric and elemental analysis. The new method represents a convenient and cost-effective way to obtain some very intense colored products from orange to deep purple.

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Keywords: Azobenzene, azoxybenzene, Reductive coupling reaction, IR and UV spectrometry, Thermal stability, Solubility

1. Introduction

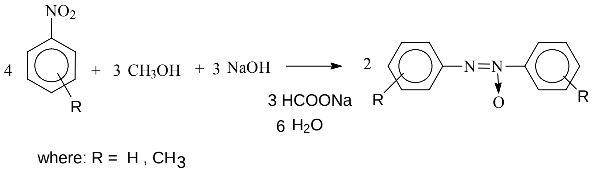
Azobenzene containing polymers are well known because they possess a wide range of properties, such as thermal and photochemical stability. Azobenzene is thermally stable up to about 350°C when kept in closed volume, although irradiation at room temperature does not cause decomposition but trans-cis isomerisation. This is the reason for the very high interest in these structures for applications in different communication technologies, non-linear optics and photoswitchable biomaterials [1]. There are a huge number of papers dealing with azobenzene containing polymers. Azobenzene chromophore can be incorporated into the polymer chain by different methods: chain growth polymerization of suitable monomers, or chromophore formation directly during the polymer synthesis as has been done with polydiazotisation [2] or the oxidative coupling reaction.

For example, some coupling reactions were reported based on various diazonium salts with copper-ammonia solutions [3], as well as the oxidative condensation of aromatic diamines in presence of oxygen and Cu_2Cl_2 and pyridine [4]. Recently a series of articles reported upon the polyrecombination of some aromatic radicals obtained by thermal or radiative splitting of aromatic bis-azides [5, 6]. On the other hand, several types of mesomorphic polymers were reported. They are thermal liquid crystalline polymers containing azoxibenzene or azobenzene groups as a mesogenic core of the main chain [7]. Both monomers were prepared by a reductive coupling of nitrobenzene derivatives [8]. Nitrobenzene derivatives produced into alkaline solution and reductive conditions various chemical species as aromatic azoxi, azo or hydrazoderivatives. Even in the case of other kind of reaction, such as the preparation of dinitrobibenzyl by a oxidative coupling reaction of p-nitrobenzene, side reaction products can often appear as aromatic azo-species [9]. The aim of this work is the study of synthesis of some aromatic azo or azoxy compounds based on a few nitrobenzene derivatives: 1,4 or 1,2-nitrotoluene, 4,6-dinitro-1,3-xylene, or 2,2'-, 2,4'-, 4,4'-dinitrodibenzyl.

2. Experimental

2.1. Materials

1,4-nitrotoluene (PNT), 1,2-nitrotoluene (ONT), 4,6-dinitro-1,3-xylene (DNX), 2,2'-, 2,4'- and 4,4'-dinitrodibenzyl (DNB), nitrobenzene (BN) were commercial products (Săvineşti, România) and were used as received. Methanol (MeOH) p.a., o-xylene p.a. and NaOH p.a. (rotulis) were used as received.



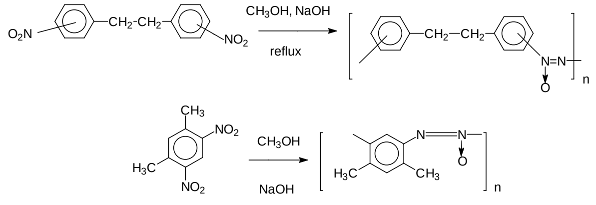
Scheme 1

Synthesis of azocompounds

A model compound was synthesised according to a published method: azoxybenzene [8, 10] (scheme 1, Table 1). A series of azoxy-compounds were obtained using a modified method. This method was adjusted following a known method for the dinitrodibenzyl preparation by oxidative coupling of the methyl group of p-nitrotoluene [11]. Firstly, a solution of natrium methoxide was prepared by refluxing for 1,5 h. To this solution nitrobenzene derivative (or the nitrocompounds) was added in a solid form or diluted in o-xylene step-wise and under stirring. The molar ratio of the three components: nitrocompound/MeOH/NaOH was of 1/1.55/1.75. Reaction mixture was maintained about 8-11 h at 96-105 °C (scheme 2). In order to maintain the homogeneousness of the mixture, various quantities of o-xylene was used as reaction solvent. At the end of reaction, the resulted solvent and water were removed by distillation. The unreacted nitrocompounds (nitrotoluenes) were also removed during the distillation. The crude product was treated with HCl solution and water in order to eliminate the anorganic salts then filtered, washed with acetone and dried. Traces of unreacted monomer were removed by the dichloroethane extraction of the main product (Soxhlet) for many hours (A1). In the case of use of the solvent, a few fractions of different colour and firmness (powder, gel) were obtained each fraction was similarly purified.

Table 1. Synthesis of azo- and azoxy derivatives.

Product	Nitro compound (g/mol)	NaOH (g/mol)	Solvent (ml)	Time (h)	Yield (g/%)
A1	PNT 54.8/0.4	28/0.7	–	9	41.5/ 91.81
A2	PNT 54.8/0.4	28/0.7	275	11	43.95/ 95.13
A3	ONT 54.8/0.4	28/0.7	–	8	24.65/ 54.53
A4	DNX 39.8/0.2	28/0.7	150	9	22.85/ 77.20
A5	4,4'-DNB 32.8/0.121	17/0.43	240	9	26.25/ 97.22
A6	2,4'-, 2,2'-DNB 54.4/0.2	30/0.75	250	8	40.9/ 91.18
M	NB 49.2/0.4	28/0.7	–	8	30.1/ 76.01



Scheme 2

Methods

IR spectra were recorded on a Perkin-Elmer Spectrometer (KBr pellets). Thermogravimetric analyses (TGA) were performed with a MOM Budapest derivatograph (in air, heating rate of 12 $°C.min^{-1}$). Differencial scanning calorimetry (DSC) was performed with a Mettler DSC 12E with a heating rate of 10 $°C. min^{-1}$ in nitrogen. Electronic absorbtion spectra were measured on a SPECORD M 42 spectrometer in DMF (soluble fractions).

3. Results and discussion

A1 compound is insoluble in almost all solvents. During the synthesis the reaction mixture was heterogeneous. In order to obtain a more homogeneous mixture we decided to use a reaction solvent (o-xylene). This goal was partially attained especially in the case of ONT, DNX and DNB. It seams that the reaction depicted in scheme 2 was not entirely in concordance with the real process. One can presume that, in fact, the reductive coupling reaction has a much more complex mechanism, as reported elsewhere [11] the reaction mechanism in the DNB synthesis based on PND consists in a several steps of reversible reactions including many types of anion, radical or anion-radical species (scheme 3). DNB synthesis take place in a suspension of PNT, NaOH and MeOH in the presence of oxygene and almost normal temperature (cca. 30°C). Methyl grups suffer an oxidative coupling reaction having as a result DNB yielding. The same reaction mixture heated at above 50 °C and in absence of oxygene can generate red-violet anion-radical (PNAR). Because of it's strong reductive abilities, this anion can cause major changes of the reaction way leading to important quantities of coloured by-products (regarding to DNB production). This is the method that we have used in our work (scheme 3 and 4). Our products are strongly coloured from orange to dark red, purple or brown. Products based on para-nitroaromatic monomers are generally insoluble powder, but the metha or orthoaromatic nitrocompounds contain several fractions with different solubilities and colour, some fraction having a gel appearance at the end of reaction.

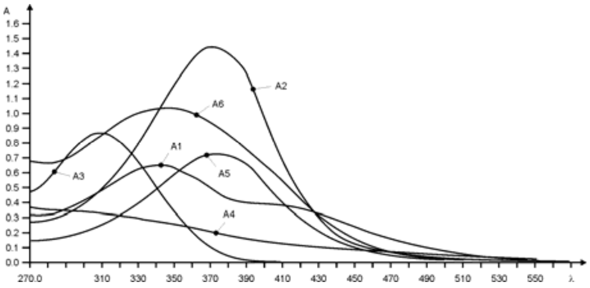
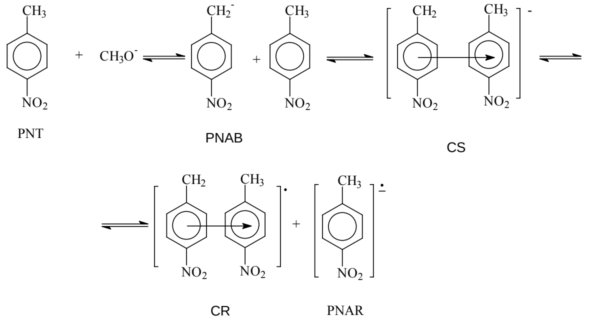
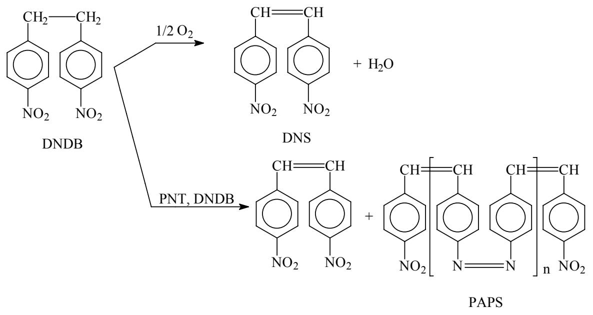


Fig. 1.

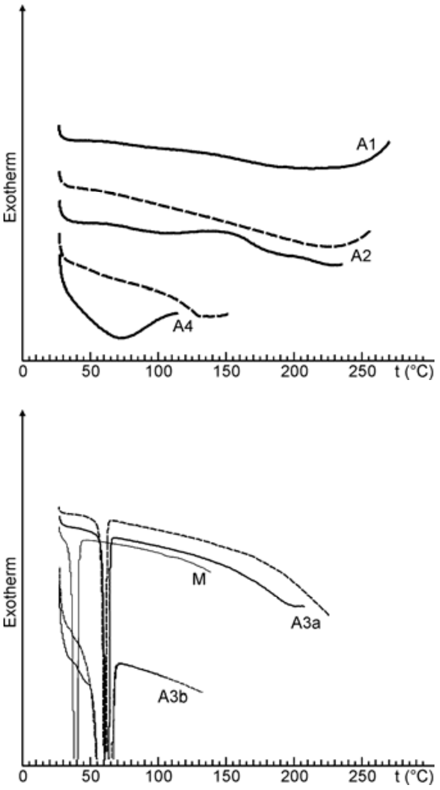


Scheme 3



Scheme 4

The IR spectrum of model compound, azoxybenzene was compared with IR spectra of the other products. IR spectral data generally confirmed the azoxy- or azobenzene structures at 1420 and 1430 cm^{-1}, but there were observed that a small part of NO_2 groups still remained in the final product. UV spectra showed, in the case A1 and A2, some differences of UV absorption bands: A1 has two absorption bands at about 343 nm and 408 nm attributed to n-π* and π -π* transitions of azobenzene chromophore and stilbene structure also. A2 presented a more intense single band, at 373 nm, than A1 band, probably due to some extensive conjugation. A3 and A4 based on ONT and DNX probably contain condensation products of methyl groups rather than azobenzene groups. However, A3 contains light fractions with azobenzene groups as shown by IR spectra.



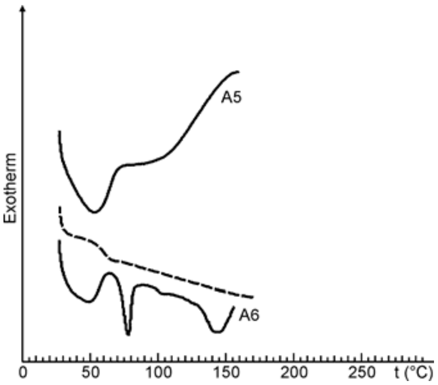


Fig. 2. DSC curves of A1, A2, A3, A4, A5, A6 and model compound M.

The thermal behavior of the products is presented in Table 2. A1 and A2 were infusible but show small endotherms and exotherms in their DSC curves. A3, A4, A6 and model compound (M) showed melting endotherms of 40 °C (M), 62 °C, 64 °C (A3a and A3b) or 78 °C (A6). A5 obtained from 4,4'-DNB presented only small endotherm (55 °C) and exotherm (160 °C) probably due to their strong packing tendency well known in the case of other polymers containing the dibenzyl system. Thermo-optical analyses were performed in order to obtain a calitative evaluation concerning melting domains.Thermal stability of all products are also presented in Table 2 and fig. One can observe that T_{10} ranged between 340-375°C except the A3 and A4. MaxDTG values of all products are of 250-295 °C depending on their chemical structures. Elemental analyses of all products presented important differences between the calculated values of ideal structure and the found values of real product that contained a complex structure as a result of reaction conditions (Table 3). Concerning the solubility of our compounds, it is remarkable that all products are almost insoluble in the most organic solvents or in strong acids.

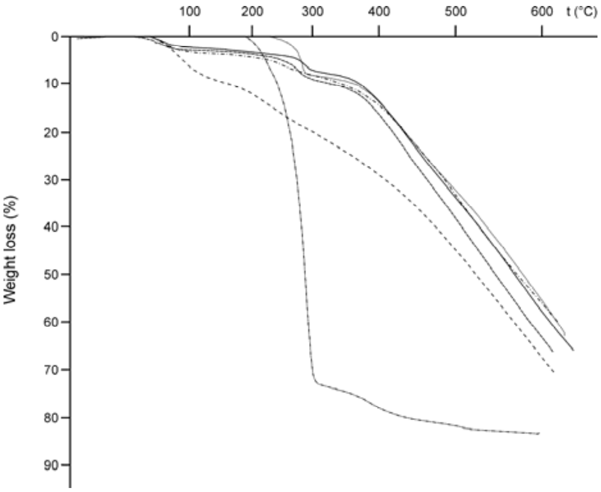


Fig. 3. Thermogravimetric curves.

Table 2. Characteristics of azo and azoxy compounds.

Product	DSC (°C) (a)			TGA (°C)	
	Endo	Tm	Exo	T_{10}	Max DTG
A1	216	–	> 250	375	295
A2	170 230	–	150	360	290
A3	195	62 64*	–	235	280
A4	70 130*	–	–	180	250
A5	55	–	> 160	340	280
A6	50.145 64*	78	–	350	260
M	–	40	–	–	–

Table 3. Elemental analysis and UV spectra.

Product	C %	H %	N %	UV spectra	
	Calculated/ Found	Calculated/ Found	Calculated/ Found	λ (nm)	A
A1	74.33/71.41	6.20/4.95	12.39/10.95	343 408	0.388 0.640
A2	74.33/71.11	6.20/5.45	12.39/11.39	373	1.435
A3	74.33/66.83	6.20/6.45	12.39/9.74	312	0.88
A4	64.86/53.93	5.40/5.09	18.92/9.20	293	0.342
A5	75.36/70.65	5.35/4.67	12.5/10.7	372	0.71
A6	75.36/71.28	5.36/5.07	12.5/9.27	346	1.03

4. Conclusions

A series of coloured products were prepared by a relative simple reductive coupling reaction. The raw materials were: 1,4-nitrotoluene (PNT), 1,2-nitrotoluene (ONT), 4,6-dinitro-1,3-xylene (DNX), 2,2'-, 2,4'- and 4,4'-dinitrodibenzyl (DNB), nitrobenzene (BN). The chosen reaction conditions have not permitted us the synthesis of well definited products. But they can be used as fills in the thermoplastic domains, as pigments in polymer compounds. As shown before, this method represents a convenient and cost-effective way to obtain some very intense colored products from orange to deep purple.

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[*] Corresponding author: nutiscor@icmpp.ro