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Studies and Charge Transport Properites of 9-N-Allylcarbazole Homologous

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Many reports are available in literature about the poly 9-N-carbazole derivatives concerning the synthesis and photoconductivity. The photoconductivity of this series of polymers has been taken a great part in many applied techniques, especially in the domain of electronics, photovoltaic effect and electro-photography. Poly allyl carbazole derivatives as donor of electrons were synthesized and the molecular orbital charges were calculated. The polymer homologous will be complexed with some electron acceptors by mixing or grafting on other macromolecules and deposited on solid surfaces as thin layers.

Key Words: Photovoltaic effect, Carbazole homologous, Electron donors and acceptors, Charge transfer, Latent images.

INTRODUCTION

Polymers in the electronic industries are overtaking long established passive roles as insulating and encapsulating materials to more active new applications. Polymers and oligomers can be used as materials for diodes, thin films transistors, light emitting diodes, photovoltaic cells and photorefractive materials. They can also be designed for microphotography applications[1]. Polymers with carbazolyl groups have been extensively studied and synthesised for different applications due to their good hole transport and luminescent properties[2]. In our laboratory, several carbazole derivatives have been synthesized and their charge transport properties have been studied[3].

EXPERIMENTAL

Molecular energy levels: A theoretical study regarding the radical and ionic polymerizations of poly allyl carbazole (9NACz) was performed

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in order to anticipate the experimental data, using the molecular orbital method; witch may indicate the more suitable polymerizations procedure. The extended Hückel non-iterative procedure method QCPE 95 EXT. HUC has been used in order to obtain the MO energy levels and set of atomic orbital coefficients for every MO. For this purpose the geometry of 9NACz molecules was given in Table-1.

TABLE-1
GEOMETRY OF N9ACz MOLECULE

Carbazole ring	Interatomic distances (Å)	Side chain	Interatomic distances (Å)
C–C	1.39	C–C	1.54
C–N	1.40	C–H	1.08
C–H	1.01	C=C	1.33
		=C–H	1.01
Valence angle			
Carbazole ring 120°			
Double bond 120°			
Saturated chain 109° 28′			

Carbazole ring is supposed to be the *x-y* plane while the vinyl group in *y-z* one.

The calculation was performed on a FELIXC-256 computer. It is known that in the static method, the total charge distribution represents a criterion for the reactivity estimation. In order to have an overall picture of this quantity the total charges on each atom are presented in Fig. 1.

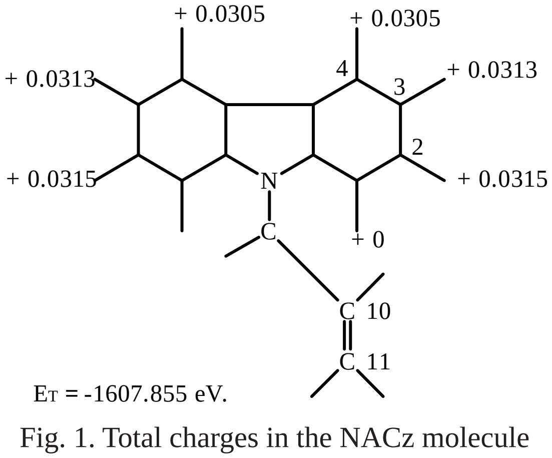

Fig. 1. Total charges in the NACz molecule

It may be observed that the C_1-C_4 carbon atoms in the carbazole ring are negatively charged which suggests the possibility of an electrophilic attack. For a charge controlled reaction with an electrophilic reagent, the following order of the reactivity from the total charge values may be assumed : $C_{11} > C_1 > C_3 > C_4 > C_2 > C_{10}$. The same atoms are deposited in an inverse order in a charge controlled reaction with electrophilic reagents[2,3]. To obtain more accurate results on the ionic polymerizations of ACz, the study of the interaction between the ACz- molecule with ACz - cation and ACz - anion was carried out.

The geometries of ACz-cation and ACz-anion used in the calculation are similar to the ACz molecule excepting the double bond. The C_{11} atom is tetrahedral in both ACz-ions. The bond length of single C_{10}–C_{11} bond is 1.50 Å and C_{10} is trigonal. Through a proton or hydride ion addition to ACz- molecule, the ACz-ions were formed.

Figs. 2 and 3 present the total atomic charges in the ACz-cation and ACz-anion, respectively. From the special representation of these molecular species, the interactions occur between C_{11} (Px orbital) from cation (anion) and C_{10}, C_{11} (Px orbital) or C_1, C_2 ....C_4 (Px orbital) from ACz. The interaction are considered to be donor accepter type. Thus, the following equation from the perturbation theory can be applied:

$$\Delta E = \frac{q_a q_b}{R_{ab}\varepsilon} + 2\sum_r \sum_s \frac{(C_{ra}C_{sb}\beta)^2}{E_r^* - E_s^*}$$

where: q_a and q_b are the total charges of the interacting atoms **a** of donor R and **b** of acceptor **S**; ε - the effective dielectric constant of the medium; R_{ab} - the distance between the two atoms **a** and **b**; $\mathbf{C_{ra}}$-the coefficients of the atomic orbital **a** in the occupied molecular orbital **S**; $\boldsymbol{\beta_{ab}}$-the resonance integral between the interacting atomic orbital **a** and **b**; E_r^* , E_s^*-quantities related to the energy of the molecular orbital **r** and **s** of the isolated R and S molecules.

Using this equation, the interaction energies ΔE are calculated. The E_r^* and E_s^* energies were replaced by the energies of molecular orbital E_r and E_s, respectively. Other considered values are as follows:

$R_{ab} = R_{cc} = 2.5$ Å and $\beta ab = \beta_{cc} = 2.63$ eV

The above mentioned data bring a contribution to the study of the properties of 9-N-allyl carbazole.

Polymerization and preparation of complexes: During the past decade, a significant amount of research has been done on dynamics of photo induced electron transfer in both protein and molecular system due to their importance in photochemical conversion and storage of energy. A number of covalently linked donor-acceptor dyads, triads, tetrads, *etc*., have been designed and studied for this purpose[4].

The polymeric materials are formed like all organic systems of molecules in condensed phase. Many polymers have been formed from unsaturated compounds like ethylene, styrene, *etc*. These unsaturated compounds have π conjugated systems, especially in carbon chains hybridized in *sp*^{2}.

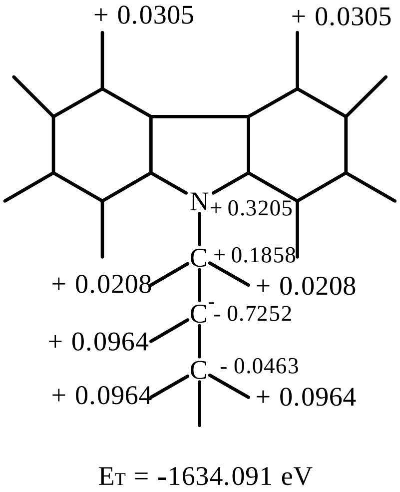

Fig. 2. Total atomic charges in the ACz-*anion*

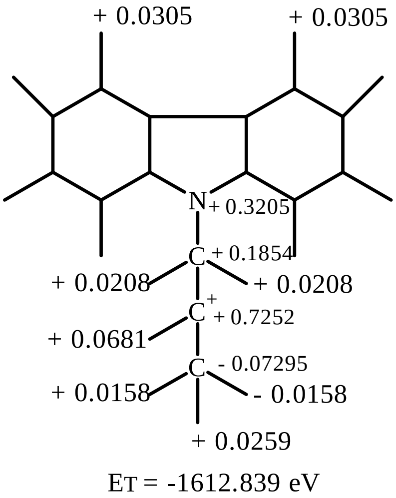

Fig. 3. Total atomic charges in the ACz-*cation*

The formation of charge transfer complex, electron conduction necessitates the possibility of creation of free charge carriers. To the molecular level, this implies easy ionization by the ejection of electron from the highest occupied orbital of the molecule (HOMO) or by the capture of electron in the lowest unoccupied molecular orbital (LUMO). Poly allyl carbazole derivatives are some of this π conjugated systems.

Monomer and polymer: Poly 9-N-allylcarbazole (*p*-9-N-ACz) was obtained by the reaction of the allyl bromide and sodium carbazole to obtain the monomer. The monomer was polymerized by radical way for the abstention of the compound. The substituted derivatives of poly 9-N-allyl carbazole was also prepared. The substitutions were made in one and two positions in the carbazolic ring. The poly allyl carbazole halogenated in 3,6-positions presents many advantages concerning the photoconductivity power and the possibility of substituting the halogen atoms by other functional groups. In this work, we intend to present the results of the synthesis and the physico-chemical studies, in position 2 for the chlorine, bromine mono substitution and positions 3,6-di-substitution in the carbazole ring.

The synthesis of these homologous was synthesized in two steps. The first one involves the synthesis of the 3-bromo (chloro) and 3,6-dichloro carbazol[5] and then condensing the sodium or the potation salt of the substituted carbazole with the allyl bromide to obtain the allyl carbazole monomers substituted in 3 and 3,6.

Synthesis of monomers

Carbazole was purchased from Carlo Erba reagent, purified by reflux in THF and the separated solid was refluxed in absolute methanol, NaOH. All the solvents were purified as usual.

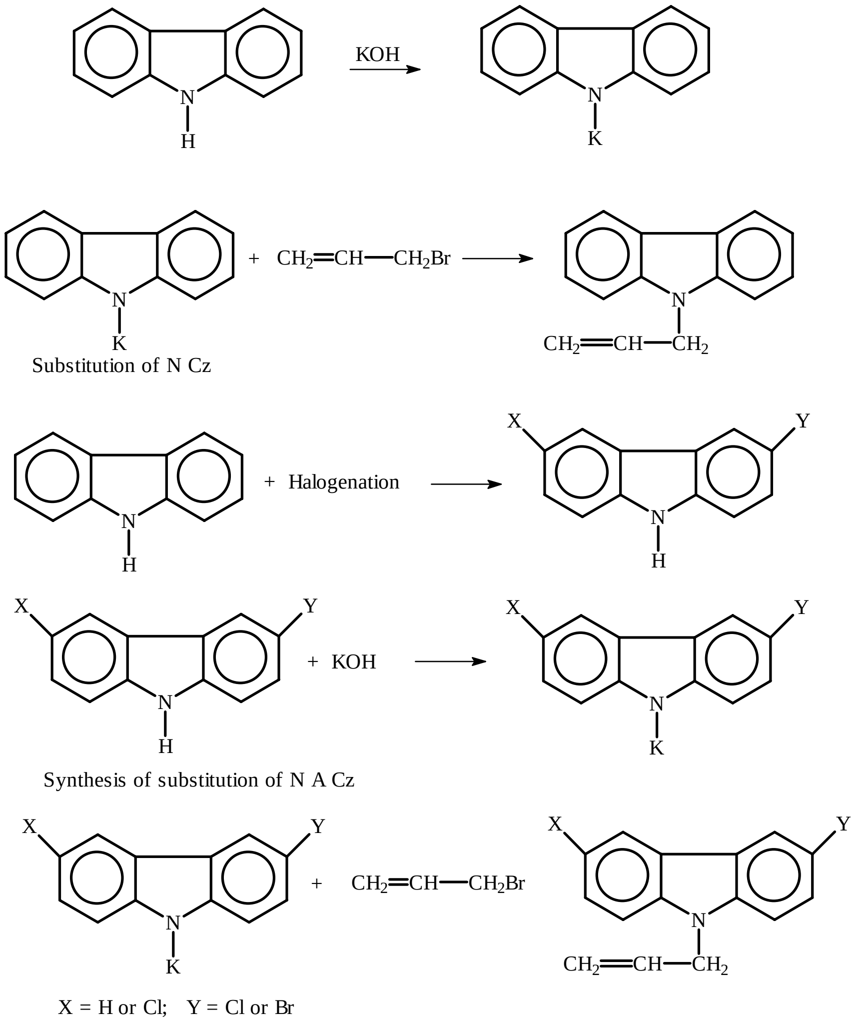

Fig. 4. Synthesis of homologous of N-9-allyl carbazole

The monomers preparation implies the synthesis of the following intermediates: 3-chloro and 3,6-dichlorcarbazole. The chlorination was performed by the use of sulfuryl chloride in chloroform as solvent medium[7].

3,6-Dibromocarbazole (DBC): The synthesis of this monomer consists of the treatment of carbazole with bromine in carbon sulphides as solvent[8].

Allyl bromides, was obtained by the treatment of the allyl alcohol with mixture of potassium bromide and dilute sulphuric acid[9].

Polymerization:

$$n \text{ monomers} + \text{catalysis} \longrightarrow \text{polymer}$$

Radical polymerizations:

$$n \text{ monomers + AIBN or DTBPO (catalysis)} \xrightarrow[\text{(toluene)}]{} \text{Polymer}$$

Anionic polymerizations:

$$n\, C_{12}XYH_6NC_3H_5 + NaH \xrightarrow[\text{(dimethylsulfoxide)}]{} [C_{12}XYH_6NC_3H_5]_n$$

Charge transfer complexes: The charge transfer complexes were synthesized by the addition of 2,3,7-trinitro fluorenone with a rapport of donor (polymer) and acceptor (10/1) by weight in THF as solvent.

$$D + A \longrightarrow A^*B^*, \text{(complex of charge transfer)}$$

The complex, as a solution, in a mixture (1 to 1) of acetone and THF; was deposited as a thin film of ≅ 1,1 mm thick on a round sheet of glass, pre-covered with argent and after deposition of the charge transfer complex, covered again with argent[10].

RESULTS AND DISCUSSION

The synthesised monomers were polymerized by anionic and radical methods analyzed by NMR and IR spectroscopy' and the molar mass (M_r) determined by viscometric method. These substituted polymers as donors, were complexed with 2,3,7-trinitro fluorenone compound, as acceptors, to produce a charge transfer complex. NMR, IR, resistivity and photoconductivity analysis proved that these complexes can be used in photoconductor in general and in electro photography, especially.

Conclusion

The above mentioned data bring a contribution to the calculation of energy levels, and the study of the properties of 9-allyl mono and di-substituted carbazoles monomers, which have been further polymerized to form charge transfer complexes.

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