Arylidene Polymers. 12. SCF-CI Molecular Orbital Studies of the Monomeric Unit of a Synthesized Poly[2,5-bis(*m*-nitrobenzylidene)cyclopentanone] Ether

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ABSTRACT: Via SCF-CI calculation it is found that the C=O oxygen atom in 2,5-bis(*p*-hydroxy-*m*-nitrobenzylidene)cyclopentanone (I) has a partially positive charge in the normal state, the oxidized form and the cation, but has a partially negative charge in the reduced form, an anion. This oxygen atom has a considerable contribution in SCF-LUMO, and, hence, it can be easily reduced. The HOMO is mainly localized over the nitro groups. The ionization potential and the electron affinity have the values 9.56 and 7.77 eV, respectively. From the π-electronic energy point of view, the trans form is more stable than the cis form. The interaction of I with 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II) in the presence of K_2CO_3 and DMAc gave the corresponding polyether III. The new polymer was confirmed by elemental analysis, IR, viscometry, DTA measurements, and X-ray analysis. The electrical conductivity measurement of III was found to be 3.4×10^{-9} Ω^{-1} cm^{-1} at 410 K.

Introduction

In recent papers, the synthesis of new arylidene polymers for semiconducting application has been reported and investigated.[1,2] Other materials synthesized include polyesters with good mechanical and thermal properties,[3-7] polyhydrazides, which possess liquid crystal character with a rigid rodlike structure,[8] polyoxadiazole and polytriazoles, characterized by interesting thermal stability behavior,[9] and polycarbonates, which have high-impact strength.[10]

A survey of the scientific literature reveals that poly(arylene ethers) are currently receiving considerable attention for potential use as engineering thermoplastics.[11,12] Several poly(arylene ethers) (PAEs), such as PEEK [poly(ether ether ketone)][13] and Vitrex PES [poly(ether sulfone)], are commercially available and are used as high-performance thermoplastics as coatings, adhesives, moldings, and composite matrix materials. The preparation of poly(arylene ethers) generally involves the nucleophilic displacement of activated aromatic dihalides in polar solvents by alkali-metal phenates via a step-growth polycondensation mechanism.[14]

We describe here the synthesis and characterization of poly(arylidene ether) with a new chemical structure. They have been synthesized by a conventional aromatic displacement route. Molecular orbital studies of its monomeric unit were carried out by SCF-CI for the purpose of increasing scientific knowledge in the development of high-performance arylidene polymers.

Results and Discussion

In a continuation of our work on the synthesis of high-performance arylidene polymers,[3-9] a new poly(arylidene ether) based on the interaction of 2,5-bis(*p*-hydroxy-*m*-nitrobenzylidene)cyclopentanone (I) and 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II) was prepared. The classical route for the synthesis of this family of macromolecules is via nucleophilic displacement of activated aromatic dihalides with potassium bisphenate in DMAc or DMSO.[14,15] A new activated arylidene monomer I and dihalides II were prepared and used for the synthesis of the arylidene ether. Nitration of 2,5-bis(*p*-hydroxybenzylidene)cyclopentane with sodium nitrite in the presence of concentrated sulfuric acid at 0 °C (a modified method for phenol nitration)[2] afforded 2,5-bis(*p*-hydroxy-*m*-nitrobenzylidene)cyclopentanone in a good yield, 75%, as depicted in Scheme I.

Interaction of I with activated arylidene dihalide 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II), which had been prepared in a previous work[2] by a step-growth polycondensation pathway, in DMAc, anhydrous potassium carbonate, and a toluene system at 170 °C gave the corresponding poly(arylidene ether) III in quantitative yield as shown in Scheme II. A literature survey reveals that high molecular weight arylene ether homopolymers and copolymers have been prepared under the same conditions.[15] It is also found that arylidene ether III has an inherent viscosity value of 0.68 dL/g in a mixture of DMSO and DMAc (2:3) and a reduced viscosity value of 0.88 dL/g in H_2SO_4; hence, the synthesized polyether has a high molecular weight.

The structure of the resulting polymer was established by elemental analysis and infrared spectroscopy. The IR spectrum showed a disappearance of the hydroxyl group and the appearance of absorption bands at 1680 cm^{-1} (C=O of cyclopentanone), at 1580–1600 cm^{-1} (C=C group), and at 1240–1210 cm^{-1} (phenyl ether stretching), in addition to other characteristic absorption bands for the rest of the macromolecule. The various characteristics of the resulting polymer including solubility, thermogravimetric analysis, DTA, X-ray analysis, and electrical properties are determined and discussed. The poly(arylidene ether) III was insoluble in most organic solvents, such as phenol, cresol, $CHCl_3$, CH_2Cl_2, CCl_4, and acetone, but slightly soluble in aprotic solvents, such as DMF and NMP. It swelled and dissolved after heating in DMSO and dimethylacetamide and was freely soluble at 30 °C in a 2:3 mixture of DMSO and NMAc. In strong protic solvents such as H_2SO_4, trifluoroacetic acid, and methanesulfonic acid, the polymer is soluble.

The thermal behavior of poly(arylidene ether) III was evaluated by thermogravimetric analysis and DTA in air. The TG curve shows a small weight loss in the range of 1.5–2% at 90 °C, which is attributed to the loss of adsorbed moisture. The temperature at which 10% weight loss occurs is considered to represent polymer decomposition. The thermogram shows that the polymer starts to

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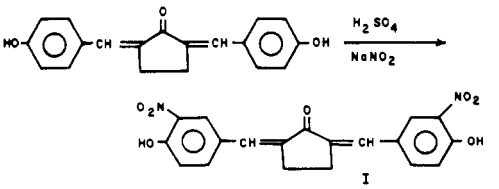
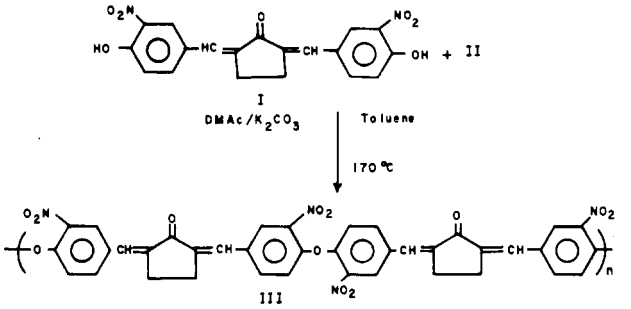
Scheme I



Scheme II



decompose at 330 °C and that above this temperature a rapid decomposition is observed.

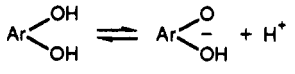
The X-ray diffractogram of polymer III shows a few reflections with an amorphous background in the region of 2θ = 5–45 °C. This indicates that the polymer is semicrystalline.

The electrical conductivity of polyether III was measured by the Arrhenius method, which gave a value of 3.2×10^{-13} Ω^{-1} cm^{-1} at 300 K. A pronounced change in the electrical conductivity was observed at 330–420 K. It increased with an increase in the temperature and reached a value of 3.4 $\times 10^{-9}$ Ω^{-1} cm^{-1} at 410 K. Above this temperature no observable change occurred.

It should be noted that the 2,5-bis(4-hydroxybenzylidene)cyclopentanone molecule has many possible structures, as represented in Figure 1. From the SCF-CI calculations[16,17] it has been concluded that the trans form has the lower π-electronic energy in the equilibrium geometry of the ground state.

From the calculated self-iterative eigenvectors of the self-iterative SCF eigenfunctions, it is concluded that the 2-oxo-1,3-cyclopentanediylidene moiety makes a substantial contribution to the HOMO and the LUMO; therefore, this moiety is sensitive to the addition or removal of an electron. The MO's highest two HOMOs and lowest two LUMOs have the symmetry species A″ in the C_s point group.

The monomer molecule can be ionized to produce an anion that can also be formed in alkaline medium. Therefore, the anionic form is responsible for the polymerization process. Therefore, it is necessary to calculate the SCF bond orders in this molecule and its anionic form.



From the SCF bond order calculations, the bond orders between the 2-oxo-1,3-cyclopentanediylidene and the benzene nuclei are strengthened in the alkaline medium. The bond orders between the benzene nuclei and the hydroxyl groups are weakened in the alkaline medium to complete the polymerization process.

The introduction of the nitro groups in positions 4 and 19 (1 and 15 in compound II) to produce 2,5-bis(4-hydroxy-3-nitrobenzylidene)cyclopentanone (I) increases the energy

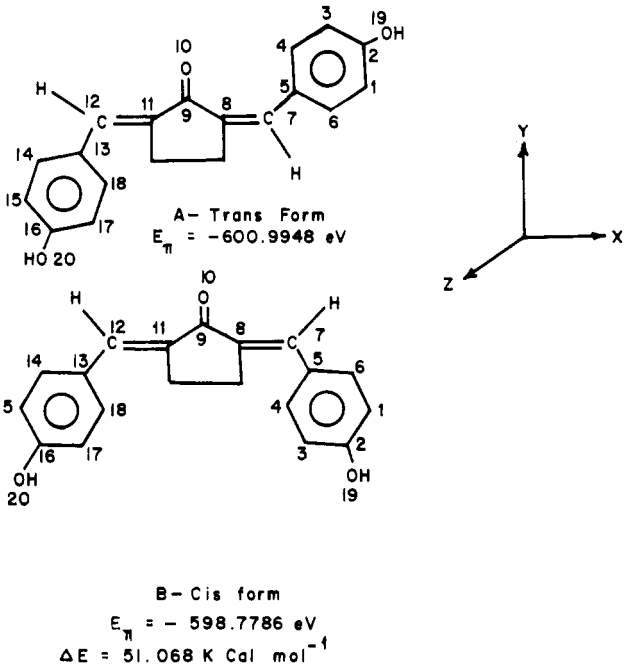


Figure 1. Possible structures of the 2,5-bis(4-hydroxybenzylidene)cyclopentanone molecule.

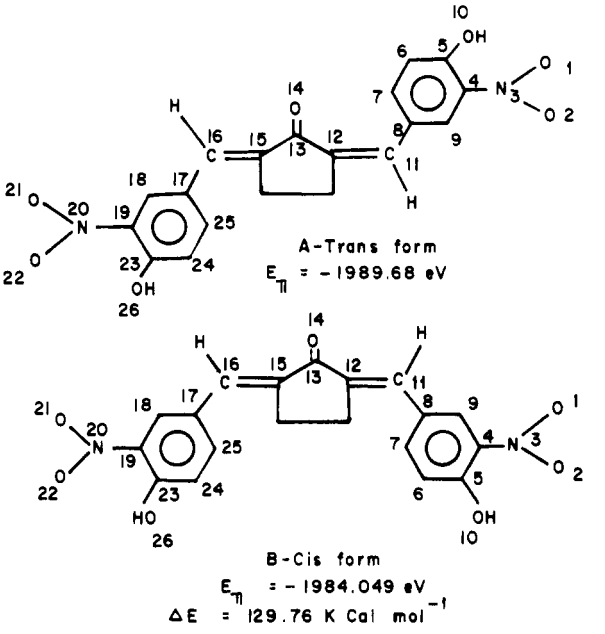


Figure 2. Energy difference between the cis and trans forms of I.

difference between the cis form and the abundant trans form from 51.068 to 129.76 kcal mol^{-1} as shown in Figure 2.

The introduction of the nitro groups in compound I increases the contribution of the carbonyl oxygen atom and the hydroxyl groups in the LUMO, and therefore they are mainly involved in the reduction process. The nitro groups in compound II make a considerable contribution in the HOMO, and, hence, they can be oxidized.

From the SCF charge density calculations, it is obvious that the charge density of the hydroxyl group in compound II is higher than that of compound I. Therefore, the hydroxyl group in compound II is more ionizable. From a general point of view, the two nitro groups withdraw electrons from the center of the molecule to produce a positive hole and two negative poles at the nitro group oxygen atoms at the edges. The carbonyl oxygen atom has a positive charge in the neutral state but gains a

Table I
State Functions and Eigenvalues of 2,5-Bis(4-hydroxybenzylidene)cyclopentanone

state function	energy, eV
$^0\Psi_1 = {}^0\Phi_1$	-600.995
$\Psi_{ex.2} = {}^t\Phi_2$	-598.675
$\Psi_{ex.3} = 0.8866707{}^t\Phi_4 - 0.4624014{}^t\Phi_3$	-598.6196
$\Psi_{ex.4} = 0.8967624{}^s\Phi_8 - 0.4425122{}^s\Phi_7$	-598.2627
$\Psi_{ex.5} = {}^s\Phi_6$	-597.8575
$\Psi_{ex.6} = {}^t\Phi_5$	-597.0162
$\Psi_{ex.7} = 0.8866707{}^t\Phi_3 + 0.4624014{}^t\Phi_4$	-596.3745
$\Psi_{ex.8} = {}^s\Phi_9$	-596.2643
$\Psi_{ex.9} = 0.8967624{}^s\Phi_7 + 0.4425122{}^s\Phi_8$	-595.9434

Table II
Electronic Transitions between the Ground State and the Excited States of 2,5-Bis(4-hydroxybenzylidene)cyclopentanone in EtOH

transition	ΔE, eV	ΔE_{nm}	M_X	M_Y	f	ΔE_{nm} (expt)
$\Psi_1 \rightarrow {}^3\Psi_{ex.2}$	2.32	535	0.000	0.644	0.084	
$\Psi_1 \rightarrow {}^3\Psi_{ex.3}$	2.375	523	-0.743	-0.362	0.142	
$\Psi_1 \rightarrow {}^1\Psi_{ex.4}$	2.732	454	-0.777	-0.388	0.180	
$\Psi_1 \rightarrow {}^1\Psi_{ex.5}$	3.138	396	0.000	0.644	0.114	398 (br)
$\Psi_1 \rightarrow {}^3\Psi_{ex.6}$	3.979	312	0.000	0.000	0.000	310 (sh)
$\Psi_1 \rightarrow {}^3\Psi_{ex.7}$	4.621	269	-1.523	-1.171	1.492	
$\Psi_1 \rightarrow {}^1\Psi_{ex.8}$	4.731	263	0.000	0.000	0.000	
$\Psi_1 \rightarrow {}^1\Psi_{ex.9}$	5.052	246	-1.506	-1.163	1.600	242

negative charge in the reduced form in alkaline medium. Therefore, the anionic form enhances the polymerization process.

Configuration interaction calculations have been carried out by using the SCF eigenvectors of the self-iterative eigenfunctions between the configuration eigenfunction of the ground state, $^0\Phi_1$, and the eight configuration eigenfunctions of the excited states, $^t\Phi_2$, $^t\Phi_3$, $^t\Phi_4$, $^t\Phi_5$, $^s\Phi_6$, $^s\Phi_7$, $^s\Phi_8$, and $^s\Phi_9$. Table I contains the state functions of the electronic transitions between the highest two HOMOs and the lowest two LUMOs. The configuration eigenfunctions Φ_2 and Φ_6, Φ_3 and Φ_7, Φ_4 and Φ_8, and Φ_5 and Φ_9 include the electronic transitions between the following MO's: $\Psi_m \rightarrow \Psi_{m+1}$, $\Psi_m \rightarrow \Psi_{m+2}$, $\Psi_{m-1} \rightarrow \Psi_{m+1}$, and $\Psi_{m-1} \rightarrow \Psi_{m+2}$. From Table II it is clear that the band at 398 nm in different solvents is coincident with the singlet transition between the ground state Φ_1 and $\Psi_{ex.5}$ in which the electronic transition takes place between the MO's $\Psi_m \rightarrow \Psi_{m+1}$, and this electronic transition is polarized in the y-axis. The small shoulder at 310 nm corresponds to the transition between the ground state and the excited state $\Psi_{ex.6}$, which includes the electronic transitions between the MO's $\Psi_{m-1} \rightarrow \Psi_{m+2}$. This band has a low intensity because it has zero oscillator strength; i.e., the transition between Ψ_{m-1} and Ψ_{m+1} is forbidden; therefore, it appears as a very weak intense shoulder (Figure 3). This agreement of the calculated electronic transitions supports the planarity of the molecule as a whole.

Experimental Section

Measurements. The elemental analyses were done on a Perkin-Elmer 240 C instrument. The IR spectra were recorded on a Pye Unicam SP3 100 spectrophotometer using KBr pellets. ^{1}H NMR spectra were run on a Varian EM-390 90-MHz spectrometer at room temperature in CF_3COOH using TMS as the internal reference. UV-visible spectra were run on a Varian Cary 219 spectrophotometer in EtOH, MeOH, and cyclohexane. The reduced viscosities of polymer solutions (0.5 g/100 mL) in H_2SO_4 were determined at 30 °C by using a Ubbelohde suspended-level viscometer. The solubilities of the polymers were examined by using 0.02 g of polymer in 3–5 mL of solvent at room temperature. X-ray diffractograms were obtained with a Philips X-ray PW 1710 diffractometer using Ni-filtered Cu Kα radiation. Thermogravimetric analyses were carried out in air with a Du Pont Model 951, 910, and 1090 thermal analyzers at a heating rate of 10 °C/min. Pellets for electrical conductivity measurements were pressed at a constant pressure of 1000 psi using an IR die. Silver paste was used to make contacts and was sandwiched between two graphite electrodes. Conductivity was measured over a temperature range of 300–425 K using a Model 610 C Keithley electrometer.[2] The SCF-CI calculations were performed on a computer Model Copam, PC-401 Turbo.

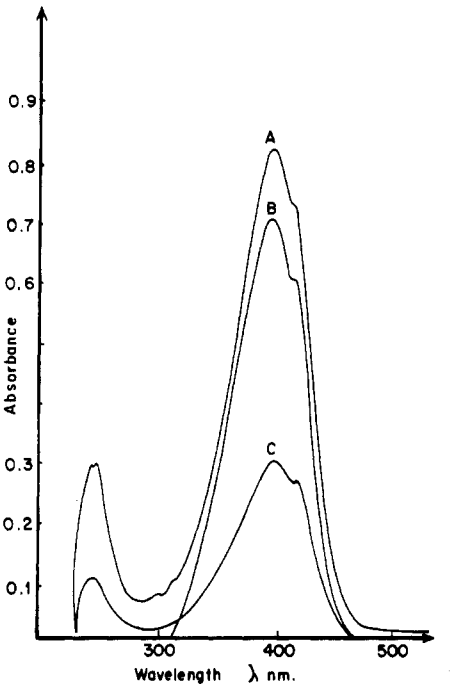


Figure 3. UV-visible spectra of 2,5-bis(4-hydroxybenzylidene)-cyclopentanone (C = 1.712 × 10^{-4} mL^{-1}): (A) ethanol, (B) methanol, (C) cyclohexane.

Reagents and Materials. Potassium carbonate, anhydrous grade (Merck), was finely powdered by using a mortar. The powdered K_2CO_3 was kept in a dry oven at 140 °C for 12 h and then heated again under reduced pressure (1 mmHg) at 100 °C for 10 h. *N,N*-Dimethylacetamide (DMAc), analytical grade (Merck), was stirred over phosphorus pentaoxide and distilled under reduced pressure in a nitrogen atmosphere. The constant boiling fraction [80–82 °C (20 Torr)] was collected and stored over molecular sieves of 5 Å. All other solvents and chemicals were very highly pure or were purified by standard methods.[4]

Monomer Synthesis. 2,5-Bis(*p*-hydroxy-*m*-nitrobenzylidene)cyclopentanone (I). To a 250-mL three-necked round-bottomed flask, fitted with a condenser and magnetic stirring bar, was added 20 mL (0.02 mol) of sulfuric acid (Analar) and 2.92 g (0.01 mol) of 2,5-bis(*p*-hydroxybenzylidene)cyclopentanone. The reaction mixture was stirred well until the solution was complete and kept at 0 °C in an ice bath for the reaction. After 15 min 1.9 g (0.02 mol) of sodium nitrite dissolved in 10 mL of water was added in a dropwise manner. After the completion of the addition, the mixture was stirred for an additional 5 h at room temperature, whereupon a reddish solid product separated out. The solid product was collected and heated in 250 mL of water at 70 °C, filtered off, washed with excess water, dried, and recrystallized from dilute acetic acid. Orange crystals were obtained in a yield of 75%, mp 243 °C. The pure sample used for the polymer synthesis was recrystallized three times and dried in vacuo (1 mmHg) at 110 °C. Anal. Calcd for $C_{19}H_{14}N_2O_7$: C, 59.58; H, 3.66; N, 7.32. Found: C, 59.72; H, 3.60; N, 7.30. IR (KBr): 3210 (s, OH group), 1680 (s, C=O group), 1580 (s, C=C group), 1330 cm^{-1} (s, CNO_2 group). ^{1}H NMR (CF_3CO_2H): δ 9.75 (s, 2 H, OH), 8 (s, 2 H, 2CH=C), 6.7–7.4 (m, 6 H, ArH), 2.5 (s, 3 H, $2CH_2$ of cyclopentanone).

2,5-Bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (II). This monomer was prepared as described in our recent work.[2]

Synthesis of Polyether III. To a 500-mL three-necked round-bottomed flask, fitted with a condenser, Dean–Stark trap, nitrogen inlet, magnetic stirring bar, and an oil bath, was added 2,5-bis(*p*-hydroxy-*m*-nitrobenzylidene)cyclopentanone (3.82 g, 0.01 mol), 2,5-bis(*p*-chloro-*m*-nitrobenzylidene)cyclopentanone (4.29 g, 0.01 mol), potassium carbonate (30 g, 0.22 mol), dimethylacetamide (DMAc; 200 mL), and toluene (210 mL). The reaction mixture was first heated to 140 °C and then to 170 °C and maintained 3 and 7 h, respectively. Toluene was used to azeotrope the water formed from the reaction. After completion of the reaction, it was allowed to cool to 75 °C, filtered through a sintered-glass funnel (G_3), and neutralized with acetic acid, whereupon a brown precipitate was formed. It was filtered off, washed several times with water and methanol, subsequently boiled in ethanol for 1 h, and again filtered off. The resulting polymer was dried in vacuo (1 mmHg) at 50 °C for 2 days. Yield: 95.1%. Anal. Calcd for $C_{38}H_{24}N_4O_{12}$: C, 62.45; H, 3.23; N, 9.43. Found: C, 62.11; H, 3.36; N, 9.62.

References and Notes

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Registry No. I, 61390-12-3; (I)(II) (copolymer), 135395-94-7; III (SRU), 135395-95-8; $NaNO_2H$, 7632-00-0; 2,5-bis(*p*-hydroxybenzylidene)cyclopentanone, 27060-66-8.