Structure-conductivity correlation in organic polymers: An MO approach

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The poor electrical conductivity of polyphenylene sulphide (PPS) has been rationalised on the basis of Pariser-Parr-Pople MO method. This approach has been extended to explain the conductivity of polyphenylene oxide (PPO). The change in conductivity of polystilbene by replacing phenylene unit with thiadiazole and thiophene units has been discussed in the light of MO calculation. However, the reported conductivities could not be rationalised on the basis of this simple MO calculation.

Of late much interest is being evinced in the synthesis of organic polymers having good electrical conductivity[1-3]. It has been generally accepted that an organic polymeric material must have an extended π-electron system to be highly conductive. Investigations have been carried out on the effect of variation of chemical structure[4] on the electrical conductivity of organic polymers. Kossmehl[4] registered a substantial increase in the conductivity from 10^{-14} to 10^{-7} ohm^{-1} cm^{-1} by replacing phenylene units by thiophene units in polyarylenevinylenes, while conductivity registered a decrease from 10^{-14} to $\sim 10^{-18}$ ohm^{-1} cm^{-1} when the phenylene units were replaced by thiadiazole units in polyarylenevinylenes.

We therefore thought it worthwhile to carry out MO calculations on these polymers. As the calculation for a complete polymer chain is practically impossible[5], we did the calculations for stilbene (I) and thiophenes (II and III) and thiadiazole derivatives (IV), which are the repeating units of the respective polymers.

Polyphenylene sulphide (PPS) is extremely low conducting[6,7]. For comparison, we extended the MO calculation on PPS (V) and its oxygen analogue, polyphenylene oxide, PPO (VI). Amongst the polymers mentioned in the present study, PPS was subjected to valence effective hamiltonian study by Bredas et al.[8], which is some sort of a band structure calculation.

Method of Calculation

In this investigation Pariser-Parr-Pople (PPP) technique without configuration interaction, known to produce satisfactory results for the π-system[9] was employed. The Fock matrix elements within the framework of PPP method are[10,11]:

$$F_{\mu\mu} = U_{\mu} + 0.5 P_{\mu\mu} \gamma_{\mu\mu} + \sum_{v \neq \mu} (P_{vv} - Z_v) \gamma_{\mu v}$$

$$F_{\mu v} = \beta_{\mu v} - 0.5 P_{\mu v} \gamma_{\mu v}$$

The values of U_{μ} (valence orbital ionisation energy) and $\gamma_{\mu\mu}$ (one-centre electron repulsion integral) were taken from the literature[12]. Z_{μ} is the core charge. The Nishimoto-Mataga expression[13] was used to calculate $\gamma_{\mu v}$, the two-centre repulsion integral. The following values were used for the resonance integral, $\beta_{\mu v}$: $\beta_{CC} = -2.30$ eV, $\beta_{CS} = -1.80$ eV, $\beta_{CN} = -2.40$ eV, $\beta_{CO} = -1.80$ eV.
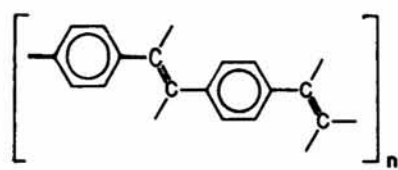
The secular equation was solved in the usual way[14] and iteration continued, until self-consistency in the bond order matrix was obtained. The bond lengths and angles of the species were obtained from the literature[15].
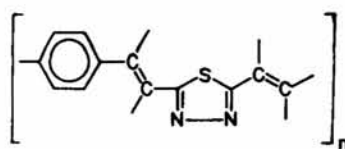
Results and Discussion

Of the occupied and unoccupied π-molecular orbitals, the frontier orbitals[16], i.e. HOMO and LUMO are the most important ones for a variety of chemical reactions.

Our working hypothesis is thus based on the premise that the conductivity of these polymers depends on the stability/instability of HOMO π-electrons[5]. In other words, the more stable (low energy) the HOMO electrons are, the less will be the conductivity. If we assume that the mechanism of conduction in these organic polymers involves the transfer of electron from π-HOMO to LUMO[17], then the conduction will depend on the HOMO energy.
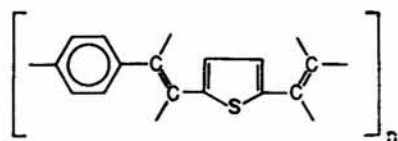
Amongst the compounds studied, PPS and PPO appear to have the most stable π-HOMOs (Table 1), the energy being -9.36 and -9.88 eV respectively. Also, worth noting is the fact that the difference of
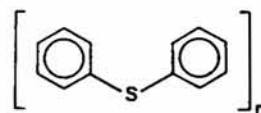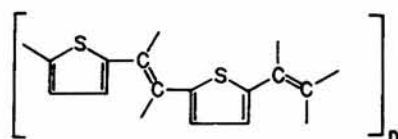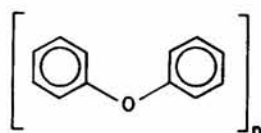
I

II

III

IV

V

VI

Table 1—HOMO and LUMO energies of repeating unit and conductivity of corresponding polymers

Compound	π-energies (eV)		Conductivity* $(\sigma)\,\Omega^{-1}\,cm^{-1}$
	HOMO	LUMO	
I	− 8.88	− 2.31	~ 10^{-14}
II	− 8.53	− 2.24	~ 10^{-7}
III	− 8.34	− 2.21	~ 10^{-8}
IV	− 9.06	− 2.46	~ 10^{-18}
V	− 9.36	− 0.95	~ 10^{-16}
VI	− 9.88	− 0.97	—

*Conductivities (σ) of compounds I to IV are taken from ref. 4, while that of V from ref. 7.

energy between HOMO and LUMO is 8.42 and 8.91 eV respectively for PPS and PPO. This is in conformity with the well documented bad conductivity (~ 10^{-16}) of PPS which is known to form zigzag chains and in addition, the phenyl rings are not coplanar[15]. Like PPS, PPO having structure similar[15] to that of PPS is expected to be a bad conductor. This is found to be so from the MO calculations. However, as the experimental results of conductivity measurements of PPO are not available no comparison could be made.

The results of MO calculation show that each of the sulphur and oxygen atoms has significant contributions to the HOMOs of PPS and PPO respectively, thereby resulting in high negative values of HOMO energy. This may be appreciated if a comparison is made with the U_μ values which are − 11.16, − 14.12, − 23.12 and − 31.42 eV respectively for $\dot{C}$, $\dot{N}$, $\ddot{S}$ and $\ddot{O}$ centres (the dot on each atom is the core charge). The results of the present investigation appear to provide an answer to the manyfold increase in the conductivity of PPO when doped with AsF_5. Sulphur atom in PPS has the highest frontier (HOMO) electron density, $2 \times (0.46)^2 = 0.42$, amongst all the atoms in this molecule and hence it is the most probable site of forming the charge transfer (CT) complex with AsF_5 which is a strong electron acceptor. The formation of CT complex will thus prevent the lone pair of sulphur from contributing to the π-HOMO in PPS. As already stated the π-HOMO in PPS is stable because of significant contribution from sulphur lone pair, consequently decrease in the contribution

from sulphur will result in increased instability of HOMO electron, thereby increasing the electron conductivity.

Although the HOMO electron density of oxygen in PPO is reasonably high $[2 \times (0.24)^2 = .115]$, other atomic centres (carbon) have higher frontier (HOMO) electron density. Hence the formation of CT complex at the oxygen atom in PPO with AsF_5 is not certain, hence the PPO doped with AsF_5 is not likely to be a good conductor.

Now in the light of the information obtained from the study of PPS and PPO, the results of polystilbene and other derivatives (I to IV) are analysed. Polystilbene (I) is reported[4] to be a poor conductor (Table 1) and the low energy (− 8.88 eV) of π-HOMO supports this view. The replacement of phenylene ring by thiadiazole is reported to decrease the conductivity by about 10^4 times (Table 1). The HOMO electrons of thiadiazole derivative (IV) having energy of

-9.06 eV, are no doubt stable. But comparable energy of HOMO and practically same ΔE value of ~ 2.60 eV $(\Delta E = E_{LUMO} - E_{HOMO})$ for both stilbene and thiadiazole derivatives makes it difficult to account for such a tremendous change in conductivity of the two systems.

It has also been noted earlier in PPS that significant contribution from sulphur lone pair stabilises the π-HOMO electrons. Interestingly in the thiadiazole derivatives (IV) such a stabilising effect is practically absent because of the insignificant contribution from sulphur to the HOMO of this compound, while each of the N atoms (each contributing one electron to π-system) has a sizeable contribution to the said molecular orbital. Since the valence orbital ionisation potentials of C and N (donating one electron) are not very much different, a large difference in the HOMO energy of stilbene and thiadiazole derivative is not expected. However, the stabilisation of π-HOMO in the thiadiazole derivative to whatever small extent, is in conformity with the difference in the U_μ values of C and N p-orbitals.

It was found[4] that replacing phenylene by thiophene enhanced the conductivity (Table 1). The repeating units containing thiophenes, e.g. II and III no doubt have HOMO whose energy is higher than that of compounds having structures I and IV. Consequently the thiophene derivatives are reasoned to be better conductors. It may be noted here again that lone pair of sulphur in thiophene contributes negligibly small to the HOMO of these thiophene derivatives and hence stabilisation of HOMO electrons as found in PPS is absent. Although, there is a difference in the HOMO energy of thiophene derivatives

and others, it remains doubtful whether such a small difference in HOMO energy and consequently in ΔE $(E_{LUMO} - E_{HOMO})$ can account for 10^6 times increase in the conductivity of thiophene derivatives.

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