

# Electrical conductivity of polySchiff bases: A theoretical study

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The electrical conductivity of poly Schiff bases obtained from benzidine-3,3'-dicarboxylic acid (BDC) with diacetyl diphenyl ether (DDE) and Glyoxal (GLY) is explained with the help of Pariser-Parr-Pople calculation. The effect of functional groups on the conduction has also been elucidated.

**Keywords** Pariser-Parr-Pople; HOMO; LUMO; electrical conductivity; polySchiff bases

## INTRODUCTION

Since the discovery of conductivity of TCNQ and its various adducts<sup>1-3</sup>, there has been widespread interest in polymeric organic conductors to displace conventional metals and inorganic materials in various applications<sup>3,4</sup>. A wealth of experimental data<sup>5,6</sup> has been accumulated for these organic conductors and a number of theories have been proposed to explain the properties of these materials, although no single simple mechanism can account for electronic conductivity in different organic conductors. There have been attempts made with different types of quantum mechanical approximations<sup>7-11</sup>, mostly band structure calculations.

In search of a simple model which is simple to comprehend and can explain the electrical conductivity of conjugated organic polymers, a few polySchiff bases were chosen as the model compounds. Electrical conductivity of polySchiff bases has been a subject of active interest for its many practical applications<sup>3</sup> and Russian workers<sup>12</sup> have noted the effect of structure on their electrical conductivity. Moreover, recent syntheses and characterizations of a new series of polySchiff bases obtained from benzidine-3,3'-dicarboxylic acid (BDC) with diacetyl diphenyl ether (DDE) and glyoxal (GLY) respectively, have been reported from this laboratory<sup>13</sup>. All these new compounds have extended conjugated chain.

The extent of delocalization of  $\pi$  electrons has a significant role in the stabilization of the conjugated system and thus in controlling the energy of the  $\pi$ -molecular orbitals of such systems<sup>14,16</sup>. Of the occupied and unoccupied  $\pi$ -molecular orbitals, the frontier orbitals, i.e. the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO) are the most important ones for a variety of chemical reactions<sup>15</sup> and electronic transitions ( $\pi \rightarrow \pi^*$  etc.)<sup>16</sup>. The difference of energy ( $\Delta E$ ) between HOMO and LUMO should, thus, approximately measure the ease of movement of electrons in the conjugated molecules. In other words  $\Delta E$  may be connected in some way to the electrical conductivity in conjugated systems.

As the calculation for a complete polymer chain is practically impossible, each of these polymers is thought

of as consisting of three blocks which are the repeating unit and the two end fragments, each block contributing in its own way to the total electrical conductivity. With this background it is thought appropriate to perform  $\pi$ -MO calculation for each fragment of some polySchiff bases employing the Pariser-Parr-Pople (PPP)<sup>17,18</sup> method which has been known to be quite effective in explaining the  $\pi$ -electronic property of conjugated systems. Here we report the preliminary findings on our attempts to correlate the electrical conductivity to the energy difference between HOMO and LUMO as discussed earlier.

## METHOD OF CALCULATION

The usual PPP method without configuration interaction has been employed. The Fock matrix elements within the framework of PPP method are<sup>17,18</sup>

$$F_{\mu\mu} = U_{\mu} + 0.5 P_{\mu\mu} v_{\mu\mu} + \sum_{\gamma \neq \mu} (P_{\nu\nu} - Z_{\nu}) \gamma_{\mu\nu}$$

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

$U_{\mu}$  is the appropriate valence orbital ionization energy,  $\gamma_{\mu\mu}$  the corresponding one-centre electron repulsion integral and  $Z_{\mu}$  the core charge. The values of  $U_{\mu}$  and  $\gamma_{\mu\mu}$  are taken from the literature<sup>19</sup>. The two centre repulsion integral  $\gamma_{\mu\nu}$  is calculated from the Nishimoto-Mataga expression<sup>20</sup>. The resonance integral ( $\beta_{\mu\nu}$ ) are transferred from related molecules. Typical values are:  $\beta_{\text{cc}(\text{ring})} = -2.40$ ,  $\beta_{\text{cc}} = -1.5$ ,  $\beta_{\text{c}(\text{ring})\text{N}} = -1.8$ ,  $\beta_{\text{c}=\text{O}} = -2.5$ ,  $\beta_{\text{c}=\text{N}} = -2.40$ ,  $\beta_{\text{c}(\equiv\text{H})} \equiv -3.0$ .

The effect of hyperconjugation of the  $-\text{CH}_3$  group is taken into account by treating  $\equiv\text{H}_3$  as a pseudo atom<sup>21</sup>. The secular equation is solved in the usual way<sup>22</sup> and interaction continued until self consistency in the bond order matrix is obtained.

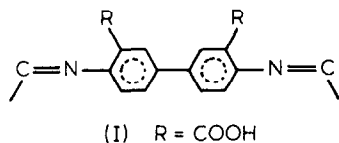
The bond lengths and angles are transferred from comparable molecules<sup>23,24</sup>. Whenever necessary resonance integrals are corrected for non planarity in the appropriate way<sup>22</sup>. Wherever two phenyl rings are di-

rectly connected, the angle between the plane of the rings are taken to be the same as in biphenyl molecule.

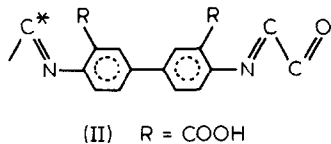
## RESULTS AND DISCUSSION

The present investigation is based on the premise that these conducting conjugated polymers may be thought of as built from three conducting blocks; the repeating unit and the two end units which are plugged to the block consisting of repeating units at appropriate places; so that the electrical conductivity of polymer will be in some way connected to the conductivity of these blocks.

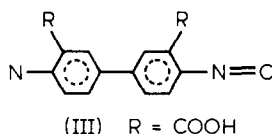
The condensation of BDC with GLX at high temperature forms a high conducting polymer (Poly I). The repeating unit is:



while the end units are:



and



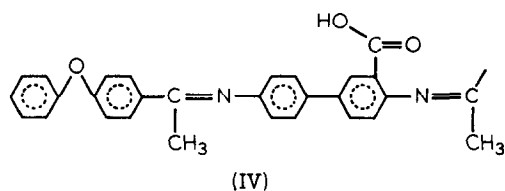
Replacement of  $-\text{COOH}$  by  $-\text{OCH}_3$  does not appreciably change, the difference in energy ( $\Delta E$ ) between  $\pi$ -HOMO and  $\pi$ -LUMO for units I and III. A difference, however, does exist for unit II; for the ( $\text{R}=\text{OCH}_3$ ) type the energy difference between  $\pi$ -HOMO and  $\pi$ -LUMO is 5.04 eV while for ( $\text{R}=\text{COOH}$ ) variety, it is 6.56 eV. This is a significant variation. And so, in polymers ( $\text{R}=\text{COOH}/\text{OCH}_3$ ) having slightly different molecular weights, the end unit corresponding to II, may have the deciding role in the electrical conduction. Accordingly, one would expect the polymer of the  $-\text{OCH}_3$  variety to be a better electrical conductor than the polymer from BDC ( $\text{R}=\text{COOH}$ ) and GLX.

The corresponding  $\pi$ -bond orders in the various units

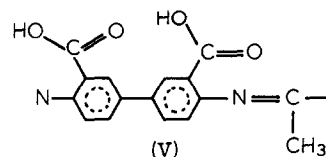
(I, II and III) for both ( $\text{R}=\text{OCH}_3/\text{COOH}$ ) types do not show any appreciable variation. It will, however, be worth noting the contribution of various atomic centres to the HOMO and LUMO in II, corresponding to  $\text{R}=\text{COOH}$  and  $\text{OCH}_3$ . The  $\pi$ -HOMO energy (II) for both  $\text{OCH}_3$  and  $\text{COOH}$  types are almost the same (Table I). In the former type the HOMO consists largely of the contributions from each of the atomic centres O, C,  $\equiv\text{H}_3$ , while the ring C-atoms are the dominant contributors for the ( $\text{R}=\text{COOH}$ ) variety. The LUMO of ( $\text{R}=\text{OCH}_3$ ) type however is  $\sim 1.4$  eV more stable than that for the ( $\text{R}=\text{COOH}$ ) variety, and also in the later, the contribution from the  $\text{C}^*$  (see II) atomic centre is practically absent, while this atom has significant contribution in the former ( $\text{OCH}_3$ ) type. This is very significant, as amongst various possible routes in conduction one may be that, at some stage of the electrical conduction the electron from HOMO of the block consisting of the repeating units is transferred to LUMO of the end unit. It is clear that the electron will find it rather difficult to travel to the end unit in  $\text{R}=(\text{COOH})$  type as the  $\text{C}^*$  atom which is the connecting link between the end fragment (II) and the repeating unit, does not have any significant contribution to the LUMO in II ( $\text{R}=\text{COOH}$ ). This also partly explains the lesser electrical conduction of polymer ( $\text{R}=\text{COOH}$ ) (Poly I) compared to  $\text{R}=\text{OCH}_3$  variety.

The condensation of BDC with DDE in two different solvents DPE\* and PPA\* gave two polymers of different electrical conductivity. Of these polymers, the one with higher conductivity will be designated as poly II and the other as poly III. The structures of the monomers suggest that probably these two polymers have the same repeating unit in different numbers. Also, the end units will be the same for both. In other words, the molecular weights of these will differ.

The repeating unit for these condensation polymer is



The energy difference ( $\Delta E$ ) between HOMO and LUMO is 6.92 eV (Table I). One end unit is



The hyperconjugation effect of  $\text{CH}_3$  was not considered in V, as this will not affect  $\Delta E$  appreciably, and therefore, V was taken to be equivalent of III. The  $\Delta E$  value for this unit is 7.22 eV.

The other end unit (VI) has  $\Delta E$  as 5.0 eV.

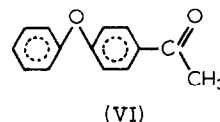


Table 1 HOMO and LUMO energies of different conducting units

Conducting unit	$\pi$ -energy (eV)		$\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$ (eV)
	HOMO	LUMO	
I R=COOH	-9.58	-2.42	7.16
R=OCH <sub>3</sub>	-9.28	-2.01	7.27
II R=COOH	-9.67	-3.11	6.56
R=OCH <sub>3</sub>	-9.57	-9.53	5.04
III R=COOH	-9.54	-2.31	7.23
R=OCH <sub>3</sub>	-8.72	-1.60	7.12
IV	-9.31	-2.39	6.92
V	-9.54	-2.31	7.23
VI	-8.13	-3.13	5.00

\* DPE = Diphenyl ether.

\* PPA = polyphosphoric acid.

Now the condensation polymer (Poly I) of BDC with GLX is more conducting (Table 2) than one of the variety (Poly III) obtained from the condensation of BDC with DDE<sup>13</sup>. Comparison of the various  $\Delta E$  values (Table 1) cannot explain this behaviour. It will not be out of place to mention here again that, only when the polymers contain more or less equal number of repeating units, the comparison of  $\Delta E$  values of repeating unit and end units will account for the conductivity. Otherwise, the extent of total conjugation in the portion consisting of repeating units cannot be compared for different polymers through the  $\Delta E$  value of just one such unit. In a series of polymers, the depth of conjugation in the entire block of repeating units will be greater for the one having more such units. It will cause a substantial reduction in the difference ( $\Delta E$ ) between HOMO and LUMO energies of this block. This may explain the better conductivities of poly I and poly II over poly III. It is unfortunate that these polymers are insoluble and their molecular weights therefore could not be determined to verify the above conjecture.

The introduction of an oxygen atom between two phenyl rings has been known to increase the electrical conductivity. This may not be surprising if one considers the low  $\Delta E$  value corresponding to VI (Table 1). However, more detailed investigation is necessary in this direction.

Tentatively it may be said that with proper consideration the electrical conductivity of conjugated polymer can be explained with the help of three conducting units, joined at appropriate places. This type of calculation, should be extended to polymers whose molecular

weights are known, so that some of the conjectures can be verified. Calculation of this type with proper empirical relation may be of great help to have an idea about molecular weights of insoluble conducting polymers. Further work in this direction is in progress.

## REFERENCES

- 1 Ferraris, J., Cowan, D. O., Walatka, V. Jr. and Perlstein, J. H. *J. Am. Chem. Soc.* 1973, **95**, 948
- 2 Garito, A. F. and Heeger, A. J. *Acc. Chem. Res.* 1974, **7**, 232
- 3 Eaton, J. E. 'Organic Semi-conducting Polymers', Marcel Dekker Inc., New York, 1970
- 4 Baughman, R. H., Bredas, J. L., Chance, R. R., Elsenbaumer, R. L. and Shacklette, L. W. *Chem. Rev.* 1982, **82**, 209
- 5 Tomkiewicz, Y. and Taranko, A. *Phys. Rev. Lett.* 1976, **36**, 751
- 6 Soda, G., Jerome, D., Weger, M., Alizon, J., Gallice, J., Robert, H., Fabre, J. M. and Giral, L. *J. Physique* 1977, **38**, 931
- 7 Suard, M., Berthier, G. and Pullman, B. *Biochem. Biophys. Acta* 1961, **52**, 254
- 8 Yomosa, S. *J. Phys. Soc. Jpn.* 1963, **18**, 1494
- 9 Berlinksky, A. J., Carolan, J. F. and Weiler, L. *Solid State Commun.* 1974, **15**, 795
- 10 Berlinksky, A. J., Carolan, J. F. and Weiler, L. *Solid State Commun.* 1976, **19**, 1165
- 11 Torrance, J. B. in 'Chemistry and Physics of One-Dimensional Metals', edited by H. J. Keller, Plenum Press, New York, 1977
- 12 Popov, Y. A., Davydov, H. E., Kubsova, N. A., Krentsel, B. A. and Kortantinov, I. I. *Polym. Sci., U.S.S.R.* 1965, **5**, 921
- 13 Suthar, B. P. and Patel, S. R. *Makromol. Chem.* 1981, **93**, 189
- 14 Streitwieser, Jr., A. 'Molecular Orbital Theory for Organic Chemists', John Wiley and Sons, 1964
- 15 Fleming, I. 'Frontier Orbitals and Organic Chemical Reactions', John Wiley and Sons, 1976
- 16 Salem, L. 'The Molecular Orbital Theory of Conjugated Systems', W. A. Benjamin, 1966
- 17 Pariser, R. and Parr, R. G. *J. Chem. Phys.* 1953, **21**, 466, 767
- 18 Pople, J. A. *Trans. Faraday Soc.* 1953, **49**, 1375
- 19 Flurry, R. L. 'Molecular Orbital Theory of Organic Molecules', Marcel Dekker, Inc., New York, 1968
- 20 Nishimoto, K. and Mataga, N. *Physikalische Chem.* 1957, **12**, 335
- 21 Linder, P. and Martenson, O. *Theor. Chim. Acta* 1967, **7**, 352
- 22 Greenwood, H. H. 'Computing Methods in Quantum Organic Chemistry', Wiley-Interscience, 1972
- 23 Bastiansen, O. *Acta Chem. Scand.* 1949, **3**, 408

Table 2 Intrinsic electrical conductivity\* of the polymers

Polymer	Intrinsic electrical conductivity (ohm <sup>-1</sup> cm <sup>-1</sup> )
BDC-DDE(DPE)	$2.0 \times 10^{-8}$
BDC-DDE(PPA)	$6.3 \times 10^{-10}$
BDC-GLY(100°)	$2.2 \times 10^{-8}$

\* Taken from ref. 13