

COMMUNICATION IV

A Simple Technique to Ascertain the Phase Relationships between the Various Atomic Orbitals in Each Pi-Molecular Orbital for the Linear Polyenes

ABSTRAK

Kaedah ringkas bagi pembentukan perhubungan fasa orbital atom 2p yang bersaling tindak (2P - AO) dalam tiap-tiap orbital molekul terhadap eletron pi (Pi-MO) dalam poliena, C_nH_{n+2} dengan julat n dan 2 ke 25 dicadangkan.

ABSTRACT

A simple technique is suggested for the construction of phase relationships of interacting 2p-atomic orbitals (2P-AO) in each molecular orbital for pi-electrons (Pi-MO) in the linear polyenes, C_nH_{n+2} with n ranging from 2 to 25.

INTRODUCTION

The organic chemists realized the power and importance of the use of Frontier Orbital Approach (Fukui, 1971) and conservation of Orbital Symmetry in discussing the mechanisms of concerted pericyclic reactions only after a series of papers published mainly by Woodward and Hoffmann in 1965 (Woodward *et al.* 1965; Hoffmann *et al.* 1965; Longuet-Higgins *et al.* 1965). The use of Frontier Orbital Approach requires the knowledge of the phase relationships of all interacting atomic orbitals in HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) or reactants. Similarly, in the construction of orbital correlation diagrams*, one requires the knowledge of the phase relationships of all interacting atomic orbitals in all molecular orbitals of the reacting systems, (Woodward *et al.* 1970; Vollmer *et al.* 1970). It is therefore quite essential for both students and teachers involved in the study of the mechanistic aspects of the concerted pericyclic reactions to construct the phase relationships of all interacting

atomic orbitals in each molecular orbital of the reacting systems.

In this paper, we describe a modified simple technique to ascertain the phase relationships of all 2p-atomic orbitals (2P-AO) in each molecular orbital for pi-electrons (Pi-MO) of linear polyenes.

CALCULATION AND DISCUSSION

Let us consider a linear polyene of general formula C_nH_{n+2} . The coefficient (c_{rj}) corresponding to the contribution of the 2 p-orbital of atom j to the rth MO (ψ_r) is given by (Coulson *et al.* 1947)

$$c_{rj} = \left(\frac{2}{n+1} \right)^{\frac{1}{2}} \sin \left(\frac{rj\pi}{n+1} \right) \quad (1)$$

where n is the total number of carbon atom in the polyene. The magnitude of c_{rj} shows the amount of contribution made by jth 2P-AO to the rth MO (ψ_r). The sign (+ or -) of c_{rj} indicates the phase relationship of interacting jth 2 P-AO in ψ_r . The positive, (+), sign of c_{rj} is considered to merely indicate that the

*Orbital correlation diagrams are usually required to establish whether the orbital symmetry was conserved during the course of the chemical transformation.

TABLE 1
The coefficients for pi-molecular orbitals (Pi-MO's) of 1, 3, 5, 7 - octatetraene

Pi-MO	←			c_j				→
ψ_r	c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8
ψ_1	0.161	0.303	0.408	0.464	0.464	0.408	0.303	0.161
ψ_2	0.303	0.464	0.048	0.161	-0.162	-0.409	-0.464	-0.302
ψ_3	0.408	0.408	0.0	-0.409	-0.408	0.0	0.409	0.408
ψ_4	0.464	0.161	-0.409	-0.302	0.304	0.407	-0.163	-0.464
ψ_5	0.464	-0.162	-0.408	0.304	0.302	-0.409	-0.159	0.464
ψ_6	0.408	-0.408	0.0	0.408	-0.409	0.0	0.407	-0.409
ψ_7	0.303	-0.464	0.409	-0.163	-0.159	0.407	-0.465	0.306
ψ_8	0.161	-0.302	0.407	-0.464	0.465	-0.410	0.306	-0.165

positive lobe of jth 2 P-OA is above the nodal plane while the negative, (-), sign of c_{ij} shows that the negative lobe of jth 2 P-AO is above the nodal plane. In order to explain it in a little more detail, we carried out the numerical operation for 1,3,5,7-octatetraene and the results are summarized in Table 1. The pictorial representation of Pi-MO, s are shown in Fig. 1.

In the use of the conservation of orbital symmetry for the mechanistic diagnosis of concerted pericyclic reactions, the signs of c_{ij} s rather than their magnitudes are very often required (Bellamy 1974). The Coulson and Longuet-Higgins equation (equation 1) can be used to calculate the values of c_{ij} and hence to ascertain the phase relationships between the various AO's in each Pi-MO's for the linear polyenes, but this technique may require a computer or a calculator for relatively larger values of n (equation 1). We wish to demonstrate in this paper a rather simple technique to ascertain the signs of all c_{ij} for a polyene, C_nH_{n+2} , with a significantly large value of n without the aid of a computer or a calculator.

It is evident from equation 1 that

$$c_{ij} = 0 \text{ if } \frac{rj}{n+1} = q \text{ with } q = 0, 1, 2, 3, \dots \dots \dots \text{any integer} \quad (2)$$

$$c_{ij} = + \text{ if } \frac{rj}{n+1} > q \text{ and } < x \text{ with } q = 0, 2, 4 \dots \dots \dots \text{any even integer and } x = 1, 3, 5 \dots \dots \dots \text{any odd integer.} \quad (3)$$

$$c_{ij} = - \text{ if } \frac{rj}{n+1} < q \text{ and } > x \quad (4)$$

Using these considerations, we have determined the signs of all coefficients for each Pi-MO of polyenes, C_nH_{n+2} , with n values ranging from 2 to 25 and the results for a few typical polyenes are summarized in Table 2. It is apparent from Table 2 that

- (i) When n is an even integer, then each row and column with odd numbering (i.e. r = j = 1, 3, 5, 7,) are symmetric and with even numbering (i.e. r = j = 2, 4, 6, 8,) are antisymmetric with respect to mirror planes passing through in between $\frac{n}{2}$ th and $(\frac{n}{2} + 1)$ th carbon atoms and Pi-MO,s respectively.
- (ii) When n is an odd integer, then each row and column with odd numbering (i.e. r = j = 1, 3, 5, 7,) are symmetric and with even numbering (i.e. r = j = 2, 4, 6, 8) are antisymmetric with respect to mirror planes passing through $(\frac{n+1}{2})$ th carbon atom and Pi-MO, respectively.

These characteristics may be summarized as below:

$$c_{rs} = (+)c_{r, n-s+1} \text{ for each value of } s, r = 1, 3, 5, \dots \dots n \text{ odd integer, and for } n \text{ odd, } s = 1, 2, 3, \dots (\frac{n-1}{2}) \quad (5)$$

TABLE 2
Phase relationships between the various atomic orbitals in pi-molecular orbital (Pi-MO) for the linear polyenes

c_n	Pi-MO Ψ_r	c_j															
		c_1	c_2	c_3	c_4	c_5	c_6	c_7	c_8	c_9	c_{10}	c_{11}	c_{12}	c_{13}	c_{14}	c_{15}	c_{16}
c_8	Ψ_1	+	+	+	+	+	+	+	+								
	Ψ_2	+	+	+	+	•	-	-	-								
	Ψ_3	+	+	0	-	•	0	+	+								
	Ψ_4	+	+	-	-	•	+	+	-								
	Ψ_5	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
	Ψ_6	+	-	-	+	•	+	-	-	+							
	Ψ_7	+	-	+	-	•	-	+	-	+							
	Ψ_8	+	-	+	-	•	+	-	+	-							
c_9	Ψ_1	+	+	+	+	•	+	+	+								
	Ψ_2	+	+	+	+	•	0	-	-	-							
	Ψ_3	+	+	+	-	•	-	-	+	+	+						
	Ψ_4	+	+	-	-	•	0	+	+	-	-						
	Ψ_5	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
	Ψ_6	+	-	-	+	•	0	-	+	+	-						
	Ψ_7	+	-	+	+	•	-	+	+	-	+						
	Ψ_8	+	-	+	-	•	0	+	-	+	-						
	Ψ_9	+	-	+	-	•	+	-	+	-	+						
c_{15}	Ψ_1	+	+	+	+	•	+	+	+	+	+	+	+	+	+	+	
	Ψ_2	+	+	+	+	•	+	+	0	-	-	-	-	-	-	-	
	Ψ_3	+	+	+	+	•	+	-	-	-	-	+	+	+	+	+	
	Ψ_4	+	+	+	0	•	-	-	0	+	+	+	0	-	-	-	
	Ψ_5	+	+	+	-	•	-	-	+	+	+	-	-	-	+	+	+
	Ψ_6	+	+	-	-	•	-	+	+	0	-	-	+	+	+	-	-
	Ψ_7	+	+	-	-	•	+	+	-	-	-	+	+	-	-	+	+
	Ψ_8	+	0	-	0	•	+	0	-	0	+	0	-	0	+	0	-
	Ψ_9	+	-	-	+	•	+	-	-	+	-	-	+	+	-	-	+
	Ψ_{10}	+	-	-	+	•	-	-	+	0	-	+	+	-	+	+	-
	Ψ_{11}	+	-	+	+	•	-	+	+	-	+	+	-	+	+	-	+
	Ψ_{12}	+	-	+	0	•	-	+	-	0	+	-	+	0	-	+	-
	Ψ_{13}	+	-	+	-	•	+	+	-	+	-	+	+	-	+	-	+
	Ψ_{14}	+	-	+	-	•	+	-	+	0	-	+	-	+	-	+	-
	Ψ_{15}	+	-	+	-	•	+	-	+	-	+	-	+	-	+	-	+
c_{16}	Ψ_1	+	+	+	+	•	+	+	+	+	+	+	+	+	+	+	+
	Ψ_2	+	+	+	+	•	+	+	+	+	-	-	-	-	-	-	-
	Ψ_3	+	+	+	+	•	+	-	-	-	-	-	-	+	+	+	+
	Ψ_4	+	+	+	+	•	-	-	-	-	+	+	+	+	-	-	-
	Ψ_5	+	+	+	-	•	-	-	+	+	+	+	-	-	-	+	+
	Ψ_6	+	+	-	-	•	-	-	+	+	-	-	+	+	+	+	-
	Ψ_7	+	+	-	-	•	+	+	+	-	-	+	+	+	-	-	+
	Ψ_8	+	+	-	-	•	+	+	-	-	+	+	-	-	+	+	-
	Ψ_9	+	-	-	+	•	+	-	-	+	+	-	-	+	+	-	+
	Ψ_{10}	+	-	-	+	•	+	-	+	+	-	-	+	-	-	+	+
	Ψ_{11}	+	-	-	+	•	-	+	+	-	-	+	+	-	-	-	+
	Ψ_{12}	+	-	+	+	•	-	+	+	-	+	-	-	+	-	-	+
	Ψ_{13}	+	-	+	-	•	-	+	-	+	-	+	-	-	+	-	+
	Ψ_{14}	+	-	+	-	•	+	+	-	+	-	+	-	-	+	-	+
	Ψ_{15}	+	-	+	-	•	+	-	+	-	+	-	+	-	+	-	+
	Ψ_{16}	+	-	+	-	•	+	-	+	-	+	-	+	-	+	-	+

$$c_{rs} = (-)c_{r, n-s+1} \text{ for each value of } s, r = 2, 4, 6, \dots n \text{ even integer and for } n \text{ even, } s = 1, 2, 3, \dots \frac{n}{2} \quad (6)$$

$$c_{sj} = (+)c_{n-s+1j} \text{ for each value of } s, j = 1, 3, 5, \dots n \text{ odd integer and for } n \text{ odd, } s = 1, 2, 3, \dots \frac{n-1}{2} \quad (7)$$

$$c_{sj} = (-)c_{n-s+1j} \text{ for each value of } s, j = 2, 4, 6, \dots n \text{ even integer and for } n \text{ even, } s = 1, 2, 3, \dots \frac{n}{2} \quad (8)$$

In equation 5 – 8, (+) and (–) merely indicate the symmetric and antisymmetric characteristics, respectively. It is apparent that for n odd, the $(\frac{n+1}{2})$ th row and column contain elements with repeat of a set of elements, +, 0, –, 0.

The symmetric and antisymmetric characteristics shown by equations 5 – 8, reveal that one quarter of the total elements of the matrix of the coefficients c_{ij} , (Table 2) for each polyene are required to generate using equations 2 – 4. The rest three quarter of the total elements may be easily generated using equations 5 – 8.

CONCLUSION

The simple technique described in this paper may be used to describe the phase relationships of all interacting atomic orbitals in each of the bonding and anti-bonding molecular orbital of pi-electrons in the linear polyene systems without calculating the absolute sign and magnitude of the coefficient of interaction of various atomic orbitals (in each molecular orbital) using equation 1.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. M.O.Agho (Chemistry Department, Bayero University) and Dr. Nordin Lajis (Chemistry Department, Universiti Pertanian) for helpful discussion and suggestions. The financial assistance from the Research and Higher Degree Committee of Bayero University is duly acknowledged.

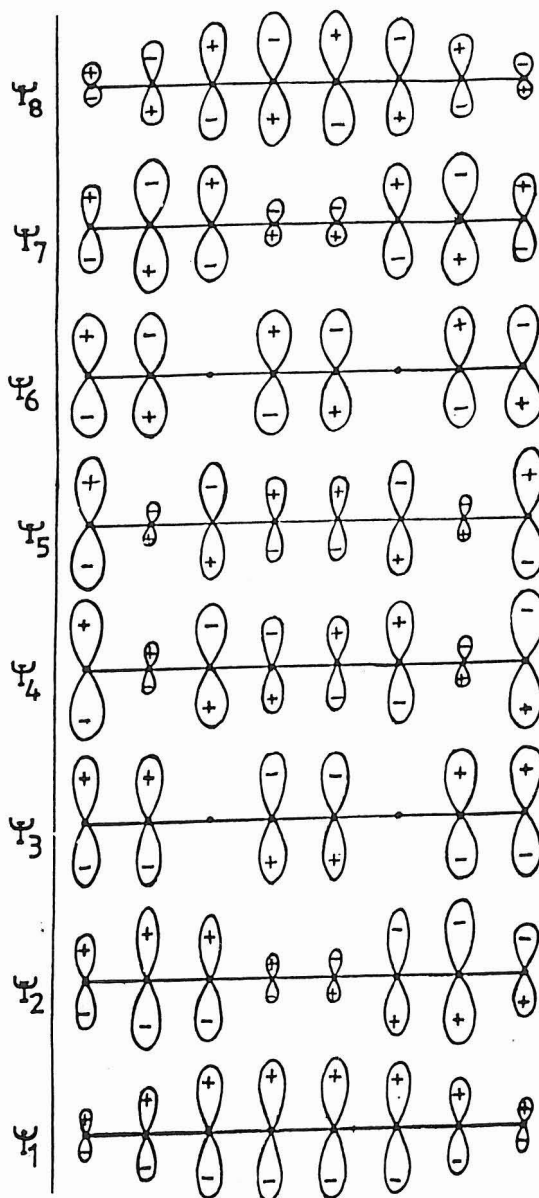


Fig. 1: Graphical representation of Pi-molecular orbitals of 1, 3, 5, 7-octatetraene as combinations of 2 P-AO's. The lengths of the orbitals are proportional to the coefficients, c_{ij} of Pi-MO's.

MOHAMAD NIYAZ KHAN

Department of Chemistry,
Bayero University, P.M.B. 3011, Kano Nigeria.

REFERENCES

BELLAMY, A.J. 1874. An Introduction to Conservation of Orbital Symmetry. Longman Text.

- COULSON, C.A. and H.C. LONGUET-HIGGINS. 1947. Electronic Structure of Conjugated Systems (I) Theory. *Proc. Roy. Soc.*, **A192**: 16
- FUKUI, K. 1971. Recognition of Stereochemical Paths by Orbital Interaction, *Acc. Chem. Res.* **4**: 57
- HOFFMANN, R. and R.B. WOODWARD. 1965. Selection Rules for Concerted Cycloaddition Reactions. *J. Amer. Chem. Soc.* **87**: 2946.
- HOFFMANN, R. and R.B. WOODWARD. 1965. Orbital Symmetries and Endo-exo Relationships in Concerted Cycloaddition Reactions. *J. Amer. Chem. Soc.* **8**: 4388
- HOFFMANN, R., and R.B. WOODWARD. 1965. Orbital Symmetries and Orientational Effects in a Sigmatropic Reaction. *J. Amer. Chem. Soc.* **87**: 4389.
- LONGUET-HIGGINS, H.C and I.W. ABRAHAMSON. 1965. The Electronic Mechanism of Electrocyclic Reactions. *J. Amer. Chem. Soc.* **87**: 2945
- VOLLMER, J.J. and K.L. SERVIS. 1970. Woodward-Hoffmann Rules: Cycloaddition Reactions. *J. Chem. Edu.* **47**: 491.
- WOODWARD, R.B. and R. HOFFMANN. 1965. Stereochemistry of Electrocyclic Reactions. *J. Amer. Chem. Soc.* **87**: 395
- WOODWARD, R.B. and R. HOFFMANN. 1965. Selection Rules for Sigmatropic Reactions. *J. Amer. Chem. Soc.* **87**: 2511.
- WOODWARD, R.B. and R. WOODMANN. 1970. The Conservation of Orbital Symmetry, Weinheim: Verlag Chemic.

(Received 29 December, 1988)