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A Simple Approach to Ascertain the Magnitudes of the Coefficients of 2 p-Atomic Orbitals in Each π-Electron Molecular Orbital of the Linear Polyenes or Polyenyl Systems.

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ABSTRAK

Pendekatan ringkas bagi mendapatkan nilai koeffisyent untuk semua orbital 2p yang bersaling tindak (2p-AO) dalam tiap-tiap orbital molekul terhadap π-elektron dalam poliena atau sistem poliena, C_nH_{n+2}, dengan julat n dari 2 ke 28 dicadangkan.

ABSTRACT

A simple approach is suggested to ascertain the magnitudes of the coefficients of all interacting 2p-atomic orbitals (2p-AO) in each π-electron molecular orbital of the linear polyenes or polyenyl systems, C_nH_{n+2}, with n ranging from 2 to 28.

INTRODUCTION

Concerted pericyclic reactions (such as electrocyclic, cycloaddition, sigmatropic rearrangement reactions etc.) are generally highly stereospecific or stereoselective. Their stereospecificity or stereoselectivity in terms of the conservation of orbital symmetry came to be understood only after a series of papers was published mainly by Woodward, Hoffmann (Woodward and Hoffmann 1965a, b; Hoffmann and Woodward 1965a, b, c) and Longuet-Hinggins)Longuet-Hinggins and Abrahamson 1965). Woodward and Hoffmann have formulated certain rules called *selection rules* which are generally used in the mechanistic generalization of these reactions. Woodward-Hoffmann *selection rules* have been derived based on molecular orbital correlation diagrams. To construct molecular orbital correlation diagrams we require the knowledge of merely the phase relationships of all interacting atomic orbitals in each molecular orbital of the reacting systems (Woodward and Hoffmann 1970; Vollmer and Servis 1970; Bellamy 1974). We have recently described a simple method to ascertain the phase relationships of all interacting 2p-atomic orbitals in each π-electron molecular orbital of linear polyenes or polyenyl systems, C_nH_{n+2}, with n ranging from 2 to 25 (Khan 1990).

Fukui has subsequently shown that Woodward-Hoffmann selection rules can be easily derived through Frontier Orbital Approach (Fukui 1971). The magnitudes of the coefficients of atomic orbitals which measure the contributions of atomic orbitals to the molecular orbitals have been shown to play an important part in the mechanistic control of several pericyclic reactions (Fleming 1976). The *regio-selectivity, site-selectivity* and *peri-selectivity* of cycloaddition reactions have been found to be greatly influenced by the signs and magnitudes of the coefficients of p-atomic orbitals in each molecular orbital.

We describe, in this paper, a simple approach to ascertain the magnitudes of all coefficients of 2p-atomic orbitals in each π-electron molecular orbital of linear polyenes or polyenyl systems.

MATERIALS AND METHODS

Electronic structural studies of linear polyenes or polyenyl systems are perhaps most clearly understood in terms of the molecular orbital theory. In a linear polyene or polyenyl system, C_nH_{n+2}, the delocalization of π-electrons involves 2p-atomic orbitals (2p-A0) of n cosecutive carbon atoms. According to the molecular orbital theory,

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such π-electron interactions yield n number of π-electron molecular orbitals which include n/2 bonding and n/2 antibonding molecular orbitals if n is an even integer and (n–1)/2 bonding, (n–1)/2 antibonding and one nonbonding molecular orbital if n is an odd integer. Linear combination of atomic orbitals method is used to construct the π-electron molecular orbitals, ψ_r, of a linear polyene or polyenyl system, C_nH_{n+2}, which may be given as

$$\psi_r = \sum_{j=1}^{n} C_{rj}\,\Phi_j \qquad r = 1, 2, 3, \ldots, n \quad (1)$$

where Φj is the jth 2p-A0 and C_{rj} represents the coefficient whose magnitude measures the contribution of jth 2p-A0 to ψ_r. The value of the square of C_{rj} (= C_{rj}^2) represents the size of the population of a π-electron of ψ_r at jth 2p-A0.

Coulson and Stewart have shown that the magnitude and sign of C_{rj} for a linear polyene or polyenyl system, C_nH_{n+2}, may be determined from equation 2 (Coulson and Stewart 1964).

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

The values of C_{rj} calculate from equation 2 are tabulated elsewhere by other workers (Streitwieser *et al*. 1965). In the calculation of C_{rj} using equation 2, one needs to calculate n^2 number of C_{rj} and hence it requires a calculator or computer for polyenes of relatively high values of n. We describe below a simple approach which requires the calculation of only n/2 (if n is an even integer) or (n+1)/2 (if n is an odd integer) number of C_{rj} with the rest C_{rj} (= $n^2 - n/2$ or $n^2 - (n+1)/2$) being generated simply by symmetry operation.

DISCUSSION

In a recent study, we have shown that for linear polyenes or polyenyl systems, C_nH_{n+2}, the sign (+ or –) of C_{rj} in each row and column of the matrix of the coefficients, C_{rj}, is symmetric with r = j = 1, 3, 5, 7, ..., an odd integer and antisymmetric with r = j = 2, 4, 6, 8, ..., an even integer, with respect to the mirror planes passing through in between (n/2)th and (([n+2]/2)th carbon atom and π-electron molecular orbitals, respectively, when n is an even integer and through ([n+1]/2)th carbon atom and π-electron molecular orbital, respectively, when n is an odd integer (Khan 1990). The calculated values of C_{rj} as shown elsewhere (Fleming 1976; Khan 1990) reveal that the symmetric and antisymmetric characteristics described above are true for both signs and magnitudes of C_{rj}.

It is evident from equation 2 that for any value of n

$$C_{rj} = C_{rj} \quad \ldots\ldots\ldots\ldots \quad (3)$$

The symmetric and antisymmetric characteristics of the elements of each row and column of the matrix of the coefficients, C_{rj}, with respect to the mirror planes as discussed above and equation 3 show that the total number of elements of the matrix $[C_{rj}]$ (r = 1, 2, 3, 4, ..., n and for each value of r, j= 1, 2, 3, 4, ..., n) required to be calculated from equation 2 is $[C_{rj}]$ with r = 1, 2, 3, 4, ..., n/2 and for each value of r, j = r, r+ 1, r + 2, r + 3, ... n/2 when n is even integer and with r = 1, 2, 3, 4, ..., (n +1)/2 and for each value of r, j = r, r + 1, r + 2, r + 3, ..., (n + 1)/2 when n is odd integer. However, as one of the reviewers has pointed out, with the well known Coulson-Rushbroke pairing theorem and with the knowledge of the properties of nodes and the symmetry of atoms in the molecules, the number of LCAO coefficients can be reduced to one quarter. Using these considerations, we have determined the magnitudes of all coefficients for each π-electron molecular orbital of polyenes, or polyenyl systems, C_nH_{n+2}, with n values ranging from 2 to 28 and the results for a few typical C_nH_{n+2}, are summarized in Table 1 where the elements generated from equation 2 coupled with a procedure described below (equations 5-7) are underlined. It is apparent from Table 1 that where n is odd integer, the ([n+1]/2) th row and column of matrix $[C_{rj}]$ contains elements with repeat of a set of elements, $C_{1(n+1)/2}$, 0, $-C_{1(n+1)/2}$, 0.

It is evident from Table 1 that if rj can be rewritten into the following form

$$rj = d + q(n+1) \quad (4)$$

so that when this equation 4 is substituted into equation 2, we will obtain

$$C_{rj} = C_{1d} \qquad \text{if q is zero or even} \quad (5)$$

$$C_{rj} = -C_{1d} \qquad \text{if q is odd} \quad (6)$$

$$C_{rj} = 0 \qquad \text{if d = 0} \quad (7)$$

Although the coefficients, C_{rj} for non-bonding orbitals can be obtained from equations 5-7 these results which are well known and trivial can be obtained from setting r = (n+1)/2 in equation 2 so that

TABLE 1a

The coefficients of the 2p-atomic orbitals in various π-electron molecular orbitals of the linear polyenes or polyenyl systems, C_nH_{n+2}.

$C_{13}H_{15}$ ←							C_{rj} →						
ψ_r	C_{r1}	C_{r2}	C_{r3}	C_{r4}	C_{r5}	C_{r6}	C_{r7}	C_{r8}	C_{r9}	C_{r10}	C_{r11}	C_{r12}	C_{r13}
ψ_{13}	a_1	$-a_2$	a_3	$-a_4$	a_5	$-a_6$	a_7	$-a_6$	a_5	$-a_4$	a_3	$-a_2$	a_1
ψ_{12}	a_2	$-a_4$	a_6	$-a_6$	a_1	$-a_2$	0	a_2	$-a_4$	a_6	$-a_4$	a_4	$-a_2$
ψ_{11}	a_3	$-a_6$	a_5	$-a_2$	$-a_1$	a_4	$-a_7$	a_4	$-a_1$	$-a_2$	a_5	$-a_6$	$-a_3$
ψ_{10}	a_4	$-a_6$	a_2	a_2	$-a_6$	a_4	0	$-a_4$	a_6	$-a_2$	$-a_2$	a_6	$-a_4$
ψ_9	a_5	$-a_4$	$-a_1$	a_6	$-a_3$	$-a_2$	a_7	$-a_2$	$-a_3$	a_6	$-a_1$	$-a_4$	a_5
ψ_8	a_6	$-a_2$	$-a_4$	a_4	a_2	$-a_6$	0	a_6	$-a_2$	$-a_4$	a_4	a_2	$-a_6$
ψ_7	a_7	0	$-a_7$	0	$-a_7$	0	$-a_7$	0	a_7	0	$-a_7$	0	a_7
ψ_6	a_6	a_2	$-a_4$	$-a_4$	a_2	a_6	0	$-a_6$	$-a_2$	a_4	a_4	$-a_2$	$-a_6$
ψ_5	a_5	a_4	$-a_1$	$-a_6$	$-a_3$	a_2	a_7	a_2	$-a_3$	$-a_6$	$-a_1$	a_4	a_5
ψ_4	a_4	a_6	a_2	$-a_2$	$-a_6$	$-a_4$	0	a_4	a_6	a_2	$-a_2$	$-a_6$	$-a_4$
ψ_3	a_3	a_6	a_5	a_2	$-a_1$	$-a_4$	$-a_7$	$-a_4$	$-a_1$	a_2	a_5	a_6	a_3
ψ_2	a_2	a_4	a_6	a_6	a_4	a_2	0	$-a_2$	$-a_4$	$-a_6$	$-a_6$	$-a_4$	$-a_2$
ψ_1	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_6	a_5	a_4	a_3	a_2	a_1

$a_1 = 0.084$, $a_2 = 0.164$, $a_3 = 0.236$, $a_4 = 0.296$,
$a_5 = 0.341$, $a_6 = 0.368$, $a_7 = 0.378$

TABLE 1b

The coefficients of the 2p-atomic orbitals in various π-electron molecular orbitals of the linear polyenes or polyenyl systems, C_nH_{n+2}.

$C_{14}H_{16}$ ←							C_{rj} →							
ψ_r	C_{r1}	C_{r2}	C_{r3}	C_{r4}	C_{r5}	C_{r6}	C_{r7}	C_{r8}	C_{r9}	C_{r10}	C_{r11}	C_{r12}	C_{r13}	C_{r14}
ψ_{14}	a_1	$-a_2$	a_3	$-a_4$	a_5	$-a_6$	a_7	$-a_7$	a_6	$-a_5$	a_4	$-a_3$	a_2	$-a_1$
ψ_{13}	a_2	$-a_4$	a_6	$-a_7$	a_5	$-a_3$	a_1	a_1	$-a_3$	a_5	$-a_7$	a_6	$-a_4$	a_2
ψ_{12}	a_3	$-a_6$	a_6	$-a_3$	0	a_3	$-a_6$	a_6	$-a_3$	0	a_3	$-a_6$	a_6	$-a_3$
ψ_{11}	a_4	$-a_7$	a_3	a_1	$-a_5$	a_6	$-a_2$	$-a_2$	a_6	$-a_5$	a_1	a_3	$-a_7$	a_4
ψ_{10}	a_5	$-a_5$	0	a_5	$-a_5$	0	a_5	$-a_5$	0	a_5	$-a_5$	0	a_5	$-a_5$
ψ_9	a_6	$-a_3$	$-a_3$	a_6	0	$-a_6$	a_3	a_3	$-a_6$	0	a_6	$-a_3$	$-a_3$	a_6
ψ_8	a_7	$-a_1$	$-a_6$	a_2	a_5	$-a_3$	$-a_4$	a_4	a_3	$-a_5$	$-a_2$	a_6	a_1	$-a_7$
ψ_7	a_7	a_1	$-a_6$	$-a_2$	a_5	a_3	$-a_4$	$-a_4$	a_3	a_5	$-a_2$	$-a_6$	a_1	a_7
ψ_6	a_6	a_3	$-a_3$	$-a_6$	0	a_6	a_3	$-a_3$	$-a_6$	0	a_6	a_3	$-a_3$	$-a_6$
ψ_5	a_5	a_5	0	$-a_5$	$-a_5$	0	a_5	a_5	0	$-a_5$	$-a_5$	0	a_5	a_5
ψ_4	a_4	a_7	a_3	$-a_1$	$-a_5$	$-a_6$	$-a_2$	a_2	a_6	a_5	a_1	$-a_3$	$-a_7$	$-a_4$
ψ_3	a_3	a_6	a_6	a_3	0	$-a_3$	$-a_6$	$-a_6$	$-a_3$	0	a_3	a_6	a_6	a_3
ψ_2	a_2	a_4	a_6	a_7	a_5	a_3	a_1	$-a_1$	$-a_3$	$-a_5$	$-a_7$	$-a_6$	$-a_4$	$-a_2$
ψ_1	a_1	a_2	a_3	a_4	a_5	a_6	a_7	a_7	a_6	a_5	a_4	a_3	a_2	a_1

$a_1 = 0.076$, $a_2 = 0.149$, $a_3 = 0.215$, $a_4 = 0.271$
$a_5 = 0.316$, $a_6 = 0.347$, $a_7 = 0.363$

$C_{rj} = r^{-1/2} (-1)^{(j-1)/2}$ if j is odd

$= 0$ if j is even*

The characteristics shown by equations 5-7 reveal that the magnitudes of n/2 (*i.e.* C_{1j} with j = 1, 2, 3, ..., n/2, when n is an even integer) or (n + 1)/2 (*i.e.* C_{1j} with j =1, 2, 3, ..., (n + 1)/2, when n is an odd integer) number of elements of the matrix of the coefficients, C_{rj}, for each polyene or polyenyl system are required to be generated using equation 2. Equations 5-7 were used to generate elements, C_{rj} with r = 2, 3, 4, ..., n/2 (if n is an even integer) or (n + 1)/2 (if n is an odd integer) and for each value of r, j = r, r + 1, r + 2, r + 3, ..., n/2 (if n is an even integer) or (n + 1)/2 (if n is an odd integer). These elements of matrix $[C_{rj}]$ are underlined as shown in Table 1 for n = 13 and 14.

We used equation 2 to calculate the magnitudes of C_{1j} with j =1, 2, 3, 4, ..., n/2 (provided n is an even integer) or (n + 1)/2 (provided n is an odd integer) for polyenes or polyenyl systems, C_nH_{n+2}, with n ranging from 3 to 28. These results are summarized in Table 2.

CONCLUSION

The results summarized in Table 2 and the simple approach described in this paper may be used to ascertain the magnitudes and sign of all coefficients, C_{rj}, of 2p-atomic orbitals, Φj, in each π-electron

TABLE 2

The coefficients of the first half of the 2p-atomic orbitals in the most stable pi-electron molecular orbitals (ψ_1) of the linear polyenes or polyenyl systems, C_nH_{n+2}.

C_nH_{n+2}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{120}	C_{121}	C_{122}	C_{123}	C_{124}
3	0.500	0.707												
4	0.372	0.602												
5	0.289	0.500	0.577											
6	0.232	0.418	0.521											
7	0.191	0.354	0.462	0.500										
8	0.161	0.303	0.408	0.464										
9	0.138	0.263	0.362	0.425	0.447									
10	0.120	0.231	0.322	0.388	0.422									
11	0.106	0.204	0.289	0.354	0.394	0.408								
12	0.094	0.182	0.260	0.323	0.367	0.389								
13	0.084	0.164	0.236	0.296	0.341	0.368	0.378							
14	0.076	0.149	0.215	0.271	0.316	0.347	0.363							
15	0.069	0.135	0.196	0.250	0.294	0.327	0.347	0.354						
16	0.063	0.124	0.181	0.231	0.274	0.307	0.330	0.342						
17	0.058	0.114	0.167	0.214	0.255	0.289	0.313	0.328	0.333					
18	0.053	0.105	0.154	0.199	0.239	0.272	0.297	0.314	0.323					
19	0.049	0.098	0.144	0.186	0.224	0.256	0.282	0.301	0.312	0.316				
20	0.046	0.091	0.134	0.174	0.210	0.241	0.267	0.287	0.301	0.308				
21	0.043	0.085	0.125	0.163	0.198	0.228	0.254	0.274	0.289	0.298	0.302			
22	0.040	0.080	0.118	0.153	0.186	0.216	0.241	0.262	0.278	0.289	0.294			
23	0.038	0.075	0.111	0.144	0.176	0.204	0.229	0.250	0.267	0.279	0.286	0.289		
24	0.036	0.070	0.104	0.136	0.166	0.194	0.218	0.239	0.256	0.269	0.278	0.282		
25	0.033	0.066	0.098	0.129	0.158	0.184	0.208	0.228	0.246	0.259	0.269	0.275	0.277	
26	0.032	0.063	0.093	0.122	0.150	0.175	0.198	0.218	0.236	0.250	0.261	0.268	0.272	
27	0.030	0.060	0.088	0.116	0.142	0.167	0.189	0.209	0.226	0.241	0.252	0.261	0.266	0.267
28	0.028	0.057	0.084	0.110	0.135	0.159	0.181	0.200	0.217	0.232	0.244	0.253	0.259	0.262

*The author is grateful to one of the reviewers for pointing this out.

molecular orbital, $\psi_r (= \sum_{j=i}^{n} C_{rj} \Phi_j$ r=1, 2, 3, 4, ..., n) of linear polyenes or polyenyl systems, C_nH_{n+2}, without the aid of a calculator or computer.

N.B. The symmetric and antisymmetric characteristics of the signs and magnitudes of the elements of each row and column of the matrix $[C_{rj}]$ with respect to a mirror plane may be defined as follows: If in the matrix $[C_{rj}]$, an element C_{rt} is the mirror image of an element C_{sj} with respect to a mirror plane, then (i) the signs of these mirror image elements are said to be symmetric or antisymmetric provided the signs of these elements (C_{rt} and C_{sj}) are the same or opposite, respectively, and (ii) the magnitudes of these elements (C_{rt} and C_{sj}) are said to be symmetric or antisymmetric provided the magnitude of C_{rt} = the magnitude of C_{sj} or the magnitude of C_{rt} = – the magnitude of C_{sj}, respectively.

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