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Simple Hückel Calculations on Acenaphth(1, 2-a) Acenaphthylene

SWAPAN KUMAR BOSE

Department of Chemistry, University College of Science, Calcutta

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The synthesis of acenaphth(1, 2-a)acenaphthylene (Fig. 1) has been reported by LETSINGER and GILPIN [1].

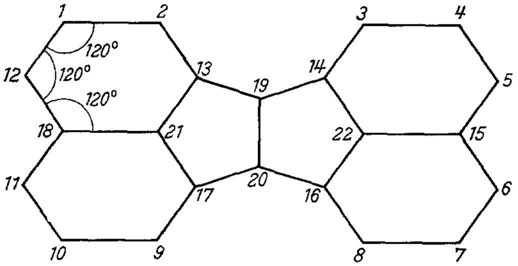

Fig. 1. Acenaphth(1,2a)acenaphthylene

Results of a simple Hückel calculation on the molecule are presented here. The assumptions are as usual. All carbon atoms are taken as equivalent. Overlap between neighbouring carbon atoms are neglected, and the coulomb and resonance integrals are taken as α and β respectively.

The symmetry group of acenaphth(1, 2-a)acenaphthylene is $D_{2h} = C_{2v} \times C_s$, so that Γ can be expressed in terms of the irreducible representations of the group C_{2v} as

$$\Gamma = 7A_1 + 4A_2 + 6B_1 + 5B_2 .$$

This enable us to factorise the secular determinant into seventh, fourth, sixth and fifth order determinants. The bases for the different representation are as follows:

A_1 $C_1 = C_7 = C_{10} = C_4$; $C_2 = C_8 = C_9 = C_3$; $C_5 = C_{11} = C_6 = C_{12}$; $C_{13} = C_{16} = C_{17} = C_{14}$; $C_{15} = C_{18}$; $C_{19} = C_{20}$; $C_{21} = C_{22}$.

A_2 $C_1 = C_7 = -C_{10} = -C_4$; $C_2 = C_8 = -C_9 = -C_3$; $C_5 = C_{11} = -C_6 = -C_{12}$; $C_{13} = C_{16} = -C_{17} = -C_{14}$; rest zero.

B_1 $C_1 = -C_7 = C_{10} = -C_4$; $C_2 = -C_8 = C_9 = -C_3$; $C_5 = -C_{11} = C_6 = -C_{12}$; $C_{13} = -C_{16} = C_{17} = -C_{14}$; $C_{15} = -C_{18}$; $C_{21} = -C_{22}$; rest zero.

B_2 $C_1 = -C_7 = -C_{10} = C_4$; $C_2 = -C_8 = -C_9 = C_3$; $C_5 = -C_{11} = -C_6 = C_{12}$; $C_{13} = -C_{16} = -C_{17} = C_{14}$; $C_{19} = -C_{20}$; rest zero.

Results

There are 22 π electrons in the molecule. These occupy the eleven lowest levels. The A.O. coefficients and energies of the occupied MO's are given in Tab. 1.

From the values of the coefficients given in Tab. 1, the electron densities q_i and bond orders $P_{r,s}$ are calculated from the relations $q_i = 2 \Sigma C_i^2$, $P_{r,s} = 2 \Sigma C_r C_s$, where C_i, C_r, C_s refer to occupied MO's (Tab. 2).

Table 1

Symmetry	A_1				A_2	
E_{MO} (β)	− 2.6736	− 1.8118	− 0.4945	− 1	− 1.6180	− 0.6181
C_1	+ 0.094	+ 0.178	+ 0.031	+ 0.289	+ 0.301	+ 0.186
C_2	+ 0.145	+ 0.028	− 0.174	+ 0.289	+ 0.301	− 0.186
C_5	+ 0.105	+ 0.295	+ 0.189	0	− 0.186	− 0.301
C_{13}	+ 0.295	− 0.128	− 0.117	0	+ 0.186	− 0.301
C_{15}	+ 0.187	+ 0.356	+ 0.062	− 0.289	0	0
C_{19}	+ 0.353	− 0.315	+ 0.463	0	0	0
C_{21}	+ 0.291	+ 0.056	− 0.347	− 0.289	0	0

Symmetry	B_1			B_2	
E_{MO} (β)	− 2.3028	− 1.3028	− 1	− 1.7746	− 1
C_1	+ 0.163	+ 0.123	+ 0.289	+ 0.237	+ 0.267
C_2	+ 0.163	− 0.123	+ 0.289	+ 0.287	0
C_5	− 0.213	− 0.283	0	+ 0.134	+ 0.267
C_{13}	+ 0.213	− 0.283	0	+ 0.273	− 0.267
C_{15}	− 0.326	− 0.245	+ 0.289	0	0
C_{19}	0	0	0	+ 0.196	− 0.267
C_{21}	+ 0.326	− 0.245	− 0.289	0	0

Table 2

charge densities		bond orders	
$q_1 = q_4 = q_7 = q_{10}$	= 1.005	$P_{1,2} = P_{3,4} = P_{7,8} = P_{9,10}$	= 0.631
$q_2 = q_3 = q_8 = q_9$	= 0.936	$P_{2,13} = P_{3,14} = P_{8,16} = P_{9,17}$	= 0.638
$q_5 = q_6 = q_{11} = {}_{12}$	= 0.946	$P_{4,5} = P_{6,7} = P_{10,11} = P_{1,12}$	= 0.705
$q_{13} = q_{14} = q_{16} = q_{17}$	= 1.026	$P_{5,15} = P_{6,15} = P_{12,18} = P_{11,18}$	= 0.550
$q_{15} = q_{18}$	= 0.998	$P_{13,21} = P_{17,21} = P_{14,22} = P_{16,22}$	= 0.516
$q_{19} = q_{20}$	= 1.095	$P_{13,19} = P_{14,19} = P_{16,20} = P_{17,20}$	= 0.430
$q_{21} = q_{22}$	= 1.083	$P_{18,21} = P_{15,22}$	= 0.531
		$P_{19,20}$	= 0.655

The energies of the highest occupied (of species A_1) and lowest unoccupied (of species B_2) MO's were corrected for overlap using the relation

$$E_{\text{Hückel}} = \alpha - m\beta$$

$$E_{\text{corrected}} = \alpha - m'\gamma$$

where $m' = \frac{m}{1 - ms}$; s being equal to 0.25 [2]. The corrected energy difference between the highest filled and lowest unfilled MO in units of γ converted to cm^{-1}

by setting $\gamma = 23000$ cm^{-1}, i. e. the longest wave length π-π^* transition has been calculated as 15020 cm^{-1}; this is compatible with the purple colour of the molecule.

The other allowed transition from the highest filled orbital of species A_1 to the lowest unoccupied orbital of species B_1, after correcting for overlap works out to 40790 cm^{-1}. This agrees fairly well with the reported value [1] of 224.5 mμ i. e. 44540 cm^{-1}.

It is difficult to comment on the positions of the molecule reactive to nucleophilic attack, on the basis of the calculated π-electron density alone; but it may be concluded that positions 19 and 20 should be most susceptible to electrophilic attack, being the positions of highest charge density. In fact, Br_2 adds to these positions with extreme ease to form a colourless dibromide [1].

The bond distances were obtained graphically from a plot of bond lengths and bond orders after the method of Coulson [3]. The bond lengths in Å are as follows:

$$D_{1,2} = 1.398, \quad D_{2,13} = 1.396, \quad D_{4,5} = 1.383, \quad D_{5,15} = 1.416, \quad D_{13,21} = 1.425$$
$$D_{13,19} = 1.444, \quad D_{18,21} = 1.420, \quad D_{19,20} = 1.393.$$

The densities of the unpaired electron in the positive and negative ions at different positions are listed below:

Table 3

Spin density of position	Anion	Cation
1, 4, 7, 10	0.004	0.001
2, 3, 8, 9	0.093	0.031
5, 6, 11, 12	0.099	0.036
13, 14, 16, 17	0.013	0.014
15, 18	0	0.004
19, 20	0.081	0.214
21, 22	0	0.121

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References

[1] Letsinger, R. L., and J. A. Gilpin: J. org. Chemistry **29**, 243 (1964).
[2] Wheland, G. W.: J. Amer. chem. Soc. **63**, 2025 (1941).
[3] Coulson, C. A.: Proc. Roy. Soc. (London) **A 169**, 413 (1939).

Dr. Swapan Kumar Bose
Dept. of Chemistry
University College of Science
Calcutta 9 (India)