Physical Parameters of Some Flavones

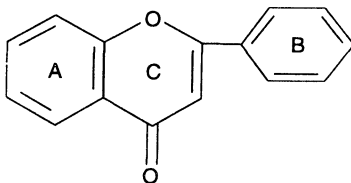K.S. SINHA*, ALKA KUMARI and P.K. RUKHAIYAR
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The colour of dye molecules is easily understood with the knowledge of its electronic structure and its effect on the light absorption in the visible and near UV region of the spectrum. The Free Electron Molecular Orbial (FEMO) approach is more relevant to the calculation of the spectral characteristics of dye molecules. The present communication deals with the calculation of λ_{max} and intensity of absorption band of some flavones.

INTRODUCTION

Flavones are yellow pigments which occur on the leaves and stems of many plants[1] in the free state or as glycosides. Being the colouring matter found in the cell-sap, hence these are known as sap-pigment. Its parent compound is 2-phenyl benzopyrone, represented as:
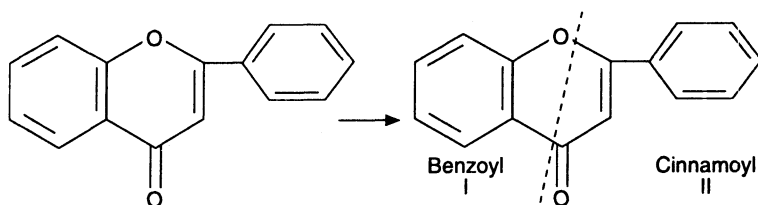
The two aromatic rings (A and B) are easily hydroxylated or methoxylated.

Much work has been done in laboratories on the chemistry of natural products, particularly those derived from plant sources such as anthocyanins, flavones[2, 3], etc. The FEMO[4, 5] (Free Electron Molecular Orbital) approach has been successful in the calculation of the spectral characteristics of flavones. Therefore the position and intensity of the absorption band of a number of flavones have been calculated. The π-electron gas system of the flavone molecule consists of 16 π-electrons contributed by the 8 double bonds and has a node in the plane of the molecule. The oxygen atom of the carbonyl group and of the pyrone ring of flavone molecule has two lone pairs of electrons. These are closely analogous to the σ-electron state[6] which lone pair electrons occupy with an antinode of the wave function in the plane of the molecule.

Flavones show three to four absorption maxima in the visible and UV region.[7] The FEMO theory is unable is account for all the observed absorption maxima since a maximum of two values for λ_{max} can be obtained. Hence for simplicity we represent the flavone molecule as consisting of two parts as shown below:

From (I) two values of λ_{max} and from (II) also two values for λ_{max} may be

Benzoyl I

Cinnamoyl II

obtained. One of the most important assumptions of FEMO theory is that the π-electrons move in a uniform potential field of one dimension. The greater electronegativity of the oxygen atom of the $>C{=}O$ group results in the accummulation of electron cloud near the oxygen atom. Thus the total number of available π-electrons gets reduced. Therefore, in this case the total number of free π-electrons is 14, 6 being distributed over I and 8 over II.

The molecular orbital diagram shows that in case of system (I) three lower energy levels are occupied by six electrons. So here the transitions are from $3 \rightarrow 4$ and $3 \rightarrow 5$, since absorptions ascribed to the jump of electrons from the highest occupied orbital to the lowest unoccupied orbital, suggested by Dale.[8] Similarly in system (II) transitions are from state $4 \rightarrow 5$ and from $4 \rightarrow 6$.

The π-electron gas extends to a distance αD_t beyond any terminal atom, where D_t is the terminal bond length and α is a constant. The average bond length l is given by

$$l = \frac{n\alpha D_t + nD_t + n_c D_c}{n + n_c}$$

Here n = total number of free ends

n_c = the number of C—C bonds

and D_C = the distance between C—C bonds

For the present calculation 7-hydroxy flavone is taken as an example showing λ_{max}[7] at 252, 268, 307 in MeOH.

Calculation

The value of α parameter of equation (I) can be calculated by comparing the energy of transition from the 4th state to 5th state of the system (II) with the energy corresponding to the absorption maxima 307 nm (*i.e.*, 6.384×10^{-12} ergs).

The energy of the transition $\Delta E_{4 \rightarrow 5}$ is

$$\Delta E_{4 \rightarrow 5} = \frac{h^2 \Delta \theta^2_{4 \rightarrow 5}}{8ml^2} \qquad (2)$$

where h = Planck's constant = 6.626×10^{-27} erg. sec.

m = mass of electron = 9.109×10^{-28} g

θ = the position of transition states for system (II);

[the values for the eight states are:

$0.056\pi, 0.225\pi, 0.333\pi, 0.350\pi, 0.649\pi, 0.666\pi, 0.774\pi, \ldots$]

By substituting $\Delta E_{4 \to 5} = 6.384 \times 10^{-12}$ erg in equation (2), the value of l may be calculated,

$$l^2 = \frac{(6.626 \times 10^{-27})^2 \times (0.649)^2 - (0.350)^2}{8 \times 9.109 \times 10^{-28} \times 6.384 \times 10^{-12}} \text{ cm}$$

or $l = 1.7 \times 10^{-8}$ cm.

The total energy of a π-electron can be regarded as the sum of the two terms $(E + \varepsilon)$ where E is the kinetic energy and can be calculated by the equation (2) and ε is the perturbation energy[6] due to the substituted functional groups having higher electronegativity than that of carbon which introduce potential wells in the linear uniform potential field of the system.

ε is given by the expression

$$\varepsilon = - A\psi^2 \tag{3}$$

where ψ is the value of the normalised wave function and A is a constant.

Here $A = 9.9 \times 10^{-20}$ erg cm.

The absorption maxima are calculated by the formula

$$\lambda = \frac{h_c}{(E + \varepsilon)_{n'} - (E + \varepsilon)_n} \tag{4}$$

where $(E + \varepsilon)_{n'}$ is the total energy of the system at excited state n' and $(E + \varepsilon)_n$ is at ground state.

The kinetic energy E of the system (II) for the transition from the $4 \to 5$ state and from $4 \to 6$ state are calculated by substituting the corresponding values of θ in equation (2), i.e.,

$$\Delta E_{4 \to 5} = \frac{h^2 \Delta \theta^2_{4 \to 5}}{8ml^2}$$

$$= \frac{(6.626 \times 10^{-27})^2 \times (0.649)^2 - (0.350)^2}{8 \times 9.109 \times 10^{-28} \times (1.7 \times 18^{-8})^2} \text{ erg}$$

$$= 6.212 \times 10^{-12} \text{ erg}$$

$$\Delta E_{4 \to 6} = \frac{h^2 \Delta \theta^2_{4 \to 6}}{8ml^2}$$

$$= \frac{(6.626 \times 10^{-27})^2 \times (0.666)^2 - (0.350)^2}{8 \times 9.109 \times 10^{-28} \times (1.7 \times 10^{-8})^2} \text{ erg.}$$

$$= 6.692 \times 10^{-12} \text{ erg}$$

The perturbation energy differences for the above transition are calculated by substituting the corresponding values of ψ in equation (3), i.e.,

$$\varepsilon = -A\psi^2$$

The values of ψ for 4th state ($= 0.350\pi$) are

$$\psi_6 = -0.1990$$

$$\psi_7 = 0.1532$$

$$\psi_8 = 0.3379$$

The values of ψ for 5th state (= 0.649 π) are

$$\psi_6 = -0.1990$$
$$\psi_7 = -0.1532$$
$$\psi_8 = 0.3379$$

The values of ψ for 6th state are

$$\psi_6 = -0.3835$$
$$\psi_7 = 0.3835$$
$$\psi_8 = 0$$

$$\therefore \quad \Delta\varepsilon_{4 \rightarrow 5} = (0.1990)^2 - (0.1990)^2 \times 9.9 \times 10^{-20} \text{ erg}$$
$$= 0$$
$$\Delta\,\varepsilon_{4 \rightarrow 6} = (0.1990)^2 - (0.3835)^2 \times 9.9 \times 10^{-20} \text{ erg}$$
$$= 1.0639 \times 10^{-12} \text{ erg}$$

The corresponding absorption maxima are

$$\lambda_{4 \rightarrow 5} = \frac{h_c}{(E + \varepsilon)_{4 \rightarrow 5}} = \frac{6.626 \times 10^{-27} \times 3 \times 10^{10}}{6.212 \times 10^{-12}} \text{ cm}$$
$$= 319 \text{ nm}$$
$$\lambda_{4 \rightarrow 6} = \frac{h_c}{(E + \varepsilon)_{4 \rightarrow 6}} = \frac{6.626 \times 10^{-27} \times 3 \times 10^{10}}{(6.692 - 1.0639) \times 10^{-12}} \text{ cm}$$
$$= 353 \text{ nm}$$

Similarly the absorption maxima corresponding to the system (I) can be calculated.

Intensity of the absorption band

Intensity of absorption band is expressed in terms of oscillator strength. Oscillator strength f is given by

$$f = \frac{8m\pi^2 C}{3h\lambda_{a \rightarrow b}}(X^2 + Y^2) \tag{5}$$

Here $\lambda_{a \rightarrow b}$ is absorption maximum of band shown by the jump of an electron of the system corresponding to wavefunction ψ_a into one with wavefunction ψ_b. X and Y are transition moments along and normal to the molecular axis and can be calculated using the electron gas wave function. The values of X and Y are
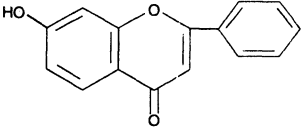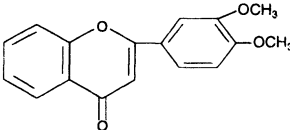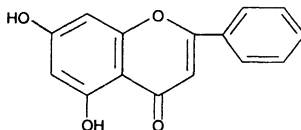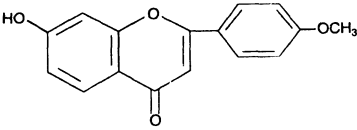
$$X = -1.0551$$
$$Y = -0.1949$$

Substituting the values of X and Y in Eqn. (4), oscillator strength is found to be

$$f = 0.4249$$

RESULTS AND DISCUSSION

The calculated values of absorption maxima are found to be in close agreement with the experimental values. The values of λ_{max} and oscillator strength (f) of some flavones are shown in Table-1.

TABLE-1

Flavone	λ_{max} (nm)		Oscillator strength (f)
	Experi-mental	Calcu-lated	
(i) 7-hydroxy flavone	307	319	0.4249
(ii) 3′,4′-dimethoxy flavone	314	318	0.3672
(iii) 5,7-dihydroxy flavone	313	316	0.3927
(iv) 4′-methoxy-7-hydroxy flavone	317	321	0.3519

ACKNOWLEDGEMENT

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