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ELECTRONIC STRUCTURES AND SPECTRA OF SOME NATURAL PRODUCTS OF THEORETICAL INTEREST—I

MOLECULAR ORBITAL STUDIES OF ANTHOCYANIDINS

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Abstract—Anthocyanidins are naturally occurring plant pigments. The HMO. ω-SCF with $\omega = 0{\cdot}5$ and $1{\cdot}4$, and Pariser–Parr–Pople semiempirical SCF ASMO CI have been employed to study the electronic properties of these compounds. In general, the results from the different methods show at least semi-quantitative consistency with respect to predictions for spectra, charge densities, and geometry of the molecules. The colors of the anthocyanidin flower pigments are explained by the PPP method in excellent agreement with the experimental data. In addition, the theoretical π-dipole moments and the directions of the transition moments have been obtained by the PPP method.

INTRODUCTION

SOME of the attractive colors which occur in plants are brought about by anthocyanidins, which are derivatives of the 2-phenylbenzopyrylium or flavylium structure (Fig. 1). These compounds cover the entire range of colors found in plants. Much work has been done on establishing the chemistry of these compounds.[2] The purpose of the present study is to characterize the nature of absorption spectra and electronic structure of these positively-charged dye molecules by means of the different MO treatments. The adequacy of the crude MO's for anthocyanidins will be examined also. Two anthocyanidin anhydrobases are also studied.

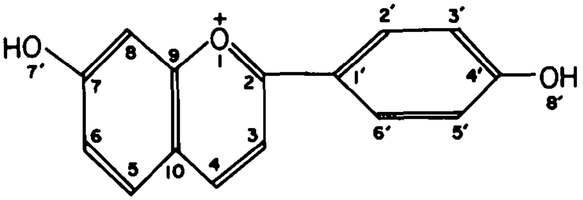

FIG. 1.

METHODS

(1) *HMO*. This method is described in detail elsewhere.[3] Two sets of Coulombic and resonance parameters were tested. Data obtained using the set of parameters recommended by Pullman and Pullmán[4] are presented in this paper, since this set of parameters was found to be more reasonable than the second set.[5,6]

(2) *ω-SCF HMO*. Wheland and Mann[7] proposed that the value of the Coulomb integral of an atom is related by $\alpha_i = \alpha_0 + (1 - q_i)\,\omega\beta_0$. Iteration until selfconsistency

(usually 5–7 iterations) was done with a new α_i. The empirical parameter ω reported has ranged from 0·33 to 1·8 (see Refs given on p. 115 of [3]). The most commonly used value is 1·4.[3,8,9] Recently, it has been shown that 0·5 fits the experimental data reasonably well, taking the electron correlation into account empirically.[10] Parameters used were the same as in the HMO.

In view of the above situation, we have examined both $\omega = 1{\cdot}4$ and 0·5. The ω-technique can be considered the simplest method for incorporating electron correlations into the HMO framework, as related by the following equation.[3 10]

$$-\omega\beta_0 = 0{\cdot}25\,(rr/rr)$$

where (rr/rr) is the one-center electron repulsion integral, and β_0 the usual resonance integral for the C—C bond.

(3) *Pariser–Parr–Pople SCF ASMO CI.* This method[11,12] in the restricted Hartree–Fock formulation was employed to calculate electronic indices, transition energies, transition moments, and oscillator strengths. The Hamiltonian, H, for the pi-electron calculation is given by Eq. (1) with readily identifiable notations.

$$H = \sum_{\mu} \left\{ -\frac{\hbar^2}{2m}\Delta\mu + V(\mu) \right\} + \sum_{\mu > \nu} \frac{e^2}{r_{\mu\nu}} \tag{1}$$

The MO, Φ_j, is approximated as the linear combination of atomic $2P_z$ orbitals (LCAO) (2):

$$\Phi_j = \sum C_{jr}\psi_r \tag{2}$$

where C_{jr} represents the r^{th} AO coefficient of the j^{th} MO. Eigenvalues are then obtained from a secular determinant (3):

$$\begin{vmatrix} F_{11} - E & F_{12} \ldots F_{1n} \\ F_{21} & F_{22} - E \ldots \\ \cdots\cdots\cdots & \cdots\cdots\cdots \\ F_{n1} & F_{n2} \ldots F_{nn} - E \end{vmatrix} = 0 \tag{3}$$

where the Fock matrix elements, F_{rs}, are given by equations (4) and (5) in the zero differential overlap approximation.

$$F_{rr} = \alpha_r + \sum_{t}^{n} P_{tt}(rr/tt) - \tfrac{1}{2}P_{rr}(rr/rr) \tag{4}$$

$$F_{rs} = \beta_{rs}^{\text{core}} - \tfrac{1}{2}P_{rs}(rr/ss) \tag{5}$$

P_{rr} and P_{rs} are respectively the diagonal and off-diagonal elements of the bond order matrix, and

$$\alpha_r = \int \psi_r(1)\left[-\frac{\hbar^2}{2m}\Delta_1 + V(1)\right]\psi_r(1)\,\mathrm{d}\tau_1 = \int \psi_r(1)\left[-\frac{\hbar^2}{2m}\Delta_1 + U_r(1)\right]\psi_r(1)\,\mathrm{d}\tau_1$$

$$+ \sum_{s \neq r} \int \left\{ \psi_r(1)\left[U_s^0(1) - \int \frac{\psi_s^2(2)\,e^2}{r_{12}}\,\mathrm{d}\tau_2\right]\right\}\psi_r(1)\,\mathrm{d}\tau_1 \cong W_{2p} - \sum_{s \neq r} P_{ss}(rr/ss) \tag{6}$$

$$\beta_{rs}^{\text{core}} = \int \psi_r(1) \left[-\frac{\hbar^2}{2m}\Delta_1 + V(1) \right] \psi_s(1)\, \mathrm{d}\tau_1 \tag{7}$$

and

$$(rr/ss) = \iint \psi_r(1)\, \psi_r(1) \frac{e^2}{r_{12}} \psi_s(2)\, \psi_s(2)\, \mathrm{d}\tau_1\, \mathrm{d}\tau_2 \tag{8}$$

Eq. (6) is the result of the Goeppert-Mayer-Sklar approximation[13] and the neglect of penetration integrals. The one-center repulsion integral, (rr/rr), was evaluated according to the Pariser-Parr approximation[11] and the two-center integral, (rr/ss), was estimated by the Mataga-Nishimoto formula.[14] Details of the numerical values of the integrals employed are tabulated in the Appendix.

RESULTS AND DISCUSSION

Fig. 1 is the numbering system which is used throughout this paper. The compounds studied are: (I) Apigenidin(5,7,4'-tri OH), (II) luteolinidin (5,7,3',4'-tetra OH), (III) pelargonidin(3,5,7,4'-tetra OH), (IV) cyanidin (3,5,7,3',4'-penta OH), (V) delphinidin(3,5,7,3',4',5'-hexa OH), (VI) an anthocyanidin anhydrobase, and (VII) cyanidine anhydrobase, the structures of which are shown in Figs 2 and 3 respectively.

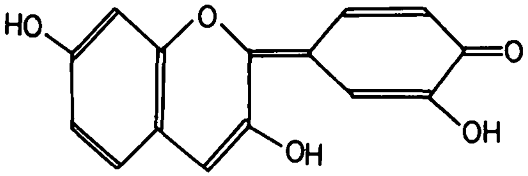

FIG. 2.

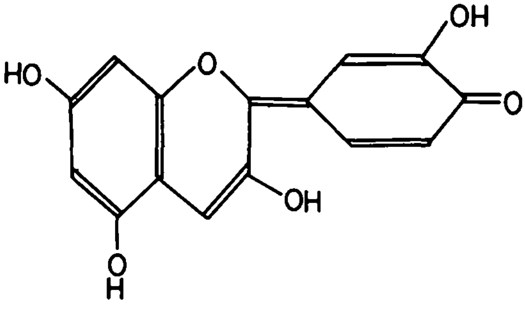

FIG. 3.

(1) *The π-electronic charge distribution.* Table 1 shows the electron density distribution of selected positions in anthocyanidins. A close examination of the table indicates that the different methods yield semiquantitatively consistent electron densities. A

TABLE 1. π-ELECTRON DENSITIES AT SELECTED POSITION*

Compound	Method	Position						
		8	7	2	1	2′	7′	8′
I	1. HMO	1·106	0·887	0·816	1·768	0·950	1·912	1·912
	2. $\omega = 0·5$	1·095	0·917	0·858	1·714	0·907	1·883	1·882
	3. $\omega = 1·4$	1·100	0·959	0·918	1·624	0·989	1·805	1·798
	4. PPP	1·131	0·974	0·615	1·929	0·916	1·758	1·768
II	1.	1·106	0·888	0·817	1·768	1·011	1·912	1·916
	2.	1·095	0·917	0·860	1·715	1·024	1·883	1·886
	3.	1·100	0·961	0·922	1·628	1·054	1·806	1·805
	4.	1·133	0·976	0·611	1·930	1·001	1·761	1·792
III	1.	1·107	0·895	0·859	1·768	0·957	1·913	1·913
	2.	1·098	0·925	0·897	1·716	0·974	1·886	1·884
	3.	1·107	0·971	0·959	1·629	0·997	1·813	1·803
	4.	1·131	0·983	0·663	1·929	0·919	1·765	1·762
	4. †	1·131	0·981	0·642	1·926	0·946	1·762	1·780
IV	1.	1·107	0·895	0·860	1·769	1·018	1·913	1·917
	2.	1·098	0·926	0·898	1·717	1·031	1·886	1·888
	3.	1·107	0·972	0·961	1·633	1·061	1·814	1·810
	4.	1·133	0·986	0·657	1·928	1·004	1·768	1·794
	4. †	1·132	0·983	0·634	1·926	1·030	1·764	1·803
V	1.	1·107	0·895	0·862	1·769	1·044	1·913	1·920
	2.	1·098	0·927	0·900	1·718	1·054	1·886	1·893
	3.	1·108	0·974	0·965	1·637	1·084	1·816	1·817
	4.	1·133	0·987	0·650	1·928	1·029	1·770	1·765
	4. †	1·131	0·984	0·627	1·925	1·061	1·766	1·827
VI	1.	1·102	0·923	0·838	1·730	0·976	1·919	1·469
	2.	1·090	0·949	0·892	1·678	1·005	1·895	1·412
	3.	1·093	0·986	0·958	1·591	1·036	1·829	1·345
	4.	1·118	1·011	0·963	1·789	0·984	1·768	1·503

* Complete molecular diagrams are available upon request.

† Non-planar conformation ($\theta = 45°$).

major discrepancy, however, can be found in the charge at position 1 ($=\overset{+}{O}-$) calculated by the crude methods and the PPP technique. The latter method indicates a significantly higher electron density at that position than the values obtained by other methods. In general, the calculated electron densities on the hydroxyl oxygen are higher by the crude MO methods than by the PPP. These differences are more apparent between the HMO and the PPP than between the ω-HMO and the latter. As expected, the site of alkali attack,[2] position 2, is seen to be positive, especially in the PPP calculation. Although electron density distributions of the anthocyanidins treated are quite similar to each other, position 2′ shows a unique feature in that only compounds I and II have slightly positive values. This suggests possible varia-

TABLE 2. SELECTED BOND DISTANCES (Å) CALCULATED FROM MOBILE BOND ORDERS

				bond		
Compound	Method	7–8	1–2	2–1′	7–8′	4′–7′
I	1. HMO	1·403	1·336	1·436	1·355	1·355
	2. $\omega = 0·5$	1·404	1·330	1·437	1·347	1·347
	3. $\omega = 1·4$	1·408	1·321	1·437	1·332	1·331
	4. PPP	1·409	1·366	1·444	1·323	1·325
II	1.	1·403	1·337	1·436	1·355	1·357
	2.	1·404	1·330	1·436	1·347	1·350
	3.	1·408	1·322	1·436	1·332	1·330
	4.	1·409	1·367	1·444	1·324	1·332
III	1.	1·402	1·337	1·435	1·355	1·356
	2.	1·403	1·331	1·436	1·348	1·350
	3.	1·406	1·323	1·436	1·334	1·332
	4.	1·408	1·366	1·442	1·325	1·326
	4. *	1·408	1·365	1·462	1·324	1·327
IV	1.	1·402	1·337	1·435	1·355	1·357
	2.	1·403	1·331	1·435	1·348	1·350
	3.	1·406	1·323	1·435	1·334	1·334
	4.	1·408	1·366	1·442	1·325	1·333
	4. *	1·408	1·364	1·461	1·324	1·334
V	1.	1·402	1·336	1·435	1·355	1·360
	2.	1·403	1·330	1·436	1·348	1·356
	3.	1·406	1·324	1·434	1·334	1·336
	4	1·408	1·366	1·442	1·325	1·339
	4. *	1·408	1·364	1·461	1·325	1·342
VI	1.	1·399	1·333	1·423	1·357	1·276
	2.	1·399	1·328	1·422	1·351	1·272
	3.	1·403	1·321	1·421	1·337	1·268
	4.	1·408	1·345	1·403	1·326	1·279

* Non-planar conformation ($\theta = 45°$).

tions of the electron density map due to the number and position of the OH substitutions. It is observed that the twisting of the two rings by 45° does not affect the electron density distribution drastically.

From the data in Table 1, the ω-HMO appears to yield more similar results than the HMO to the PPP calculations. However, it is not conclusive as to which value of ω, 0·5 or 1·4, is more reasonable. We will discuss more of this aspect later.

(2) *The molecular geometry.* Table 2 lists selected bond distances calculated from the mobile bond orders using the Nishimoto–Forster formula.[15] A qualitative agreement among the values calculated from different methods can be observed in Table 2. In fact, a good consistency is reproduced for the C—C distances by different methods. However, the PPP gives considerably longer bond distance between positions 1 and 2, as compared to the bond distances calculated by the

crude methods. The PPP predicts this bond to be analogous to the aromatic C—O-distance, while the other MO methods yield the bond distance to be in between —C=O and —C—O— distances. According to the Schomaker–Stevenson relationship,[16] the bond (—C=$\overset{+}{\text{O}}$—) distance should be shorter than the bond (—C—O—) due to the polar contraction, in favor of the bond distance calculated from the crude MO's. However, it is not possible to determine whether the values calculated by the PPP or the crude methods are correct, since the positive charge is delocalized.[17] A more detailed study should be made to investigate the dependence of the results on the choice of the various HMO parameters. Unfortunately, no experimental bond distances for these molecules are available.

Apparently, the twisting of the rings by $\theta = 45°$ does not affect the electron density distributions (Table 1) and bond distances, except the C_2—C'_1 bond. The increase in the bond distance is obviously due to the lessening of the conjugation of the two ring systems through that bond.

(3) *Resonance energies*. Table 3 summarizes values of the resonance energies (DE_π) calculated according to the definition given in Refs 3 and 4. The energy of the localized π-system is calculated by the same method and use of the same parameters as those used for the delocalized system. In view of the values calculated by the HMO, the resonance interpretation[17] based on the valence bond concept applied to flavylium pigments appears to be confirmed. DE_π per electron is the highest for apigenidin. It can be seen that the increase in OH substitutions is accompanied by the decrease in the resonance energy per electron. The values calculated by the $\omega = 0{\cdot}5$ method are considerably lower. Even negative resonance energies are obtained by the $\omega = 1{\cdot}4$ method. It appears that such negative resonance energies may have arisen from the over-emphasis of the electron correlation introduced empirically with $\omega = 1{\cdot}4$. The resonance energies can also be calculated by the PPP method in the same way as in the crude methods.[18] We have not attempted to compute the resonance energies by the PPP. An extensive investigation of resonance energies by the PPP may shed some light on the theoretical basis of the $\omega = 0{\cdot}5$ or $1{\cdot}4$ computations. However, the inadequacy of $\omega = 1{\cdot}4$ has already been pointed out.[10, 19]

TABLE 3. RESONANCE ENERGIES (IN β) OF ANTHOCYANIDINS IN THE PLANAR CONFORMATION

Compound	Method				
	HMO		$\omega(0{\cdot}5)$		$\omega(1{\cdot}4)$
	Total	Per e$^-$	Total	Per e$^-$	
I	7·1	0·323	4·6	0·209	−0·2
V	7·3	0·304	3·9	0·163	−2·5
III	7·3	0·304	3·9	0·163	−2·6
IV	7·6	0·292	3·3	0·127	−4·7
V	7·8	0·279	2·6	0·093	−6·9
VI	6·3	0·263	2·8	0·117	−3·1

(4) *Reactivity*. The simple MO methods were used for this purpose. Only brief

application of the results will be discussed here. The well-known nucleophilic attack by OH^- occurs at position 2 which is shown to be the most positive site (Table 1). It was shown that the electron density itself is not always a reliable measure of the reactivity.[5] We have previously analyzed various reactivity indices, and found that the superdelocalizabilities and localization energies are satisfactory indices for the prediction of reactive sites. From the superdelocalizabilities for electrophilic attack and the electrophilic localization energies for compounds I–V, positions 6 and 8 were found to be most active.

In the calculations for nucleophilic attack, the frontier orbital densities and superdelocalizability for nucleophilic attack (SDN), both the HMO and $\omega = 0{\cdot}5$ methods showed positions 2 and 4 to be the most reactive. However, the differences between the values at both positions were small in most cases, so that further evidence is needed to decide which position is theoretically most reactive. By looking at the localization energies, position 4 is predicted to be the most reactive ($-1{\cdot}782\ \beta$ by HMO and $-2{\cdot}392\ \beta$ by $\omega = 0{\cdot}5$ computations). This is an interesting result. It has been shown that with alkaline reagents, the flavylium skeleton is broken at the central pyroxonium ring resulting in the formation of a phloroglucinol and a benzoic acid derivative.[20] Position 2 has been known to be the most reactive position in these types of molecules, and the most probable position for the initial attack. However, the calculation also shows that position 4 is equally or more reactive, and, in fact, one product which has been proposed has a —OH group at position 4.[21] The HMO and $\omega = 0{\cdot}5$ computations gave more consistent reactivity results for compounds I–V than the $\omega = 1{\cdot}4$ method.

(5) *Dipole moments.* π-Dipole moments calculated by the PPP method are listed in Table 4. The dipole moments are reasonable in view of the fact that these are charged molecules. It can be seen that the dipole moment for luteolinidin (II) is much lower than the rest. This reflects the somewhat symmetrical —OH substitutions on this compound. Compounds VI and VII are shown to be the most polar molecules among the anthocyanidins treated.

TABLE 4. DIPOLE MOMENTS (IN DEBYE) OF ANTHOCYANIDINS

Compound	Planar	Non-planar ($\theta = 45°$)
I	3·491	
II	1·494	
III	5·130	5·350
IV	3·561	4·282
V	5·766	5·489
VI	8·324	
VII	10·740	

Slight increases (in III and IV) and a decrease (in V) in the dipole moments are obtained by the twisting of the two rings by $\theta = 45°$. No experimental ($\sigma + \pi$) dipole moments are available. However, the data presented are of use for qualitative description of the polarity of these dyes.

(6) *Electronic spectra.* Pauling qualitatively discussed colors of the anthocyanidins

in terms of the resonance concept.[17] Fig. 4 and Tables 5 and 6 present quantitative spectral data obtained in this investigation.

From Fig. 4, both the HMO and $\omega = 0{\cdot}5$ methods yield calculated λ_{max} in excellent correlation with the observed spectra. However, the $\omega = 1{\cdot}4$ results show poorer correlation. From the slopes of the plot shown in Fig. 4, $\beta_{spectroscopic} = -2{\cdot}931$ eV from the HMO and $-3{\cdot}449$ eV from the $\omega = 0{\cdot}5$ method are obtained. These values can be used for calculating λ_{max} for other anthocyanidins not treated in the present work.

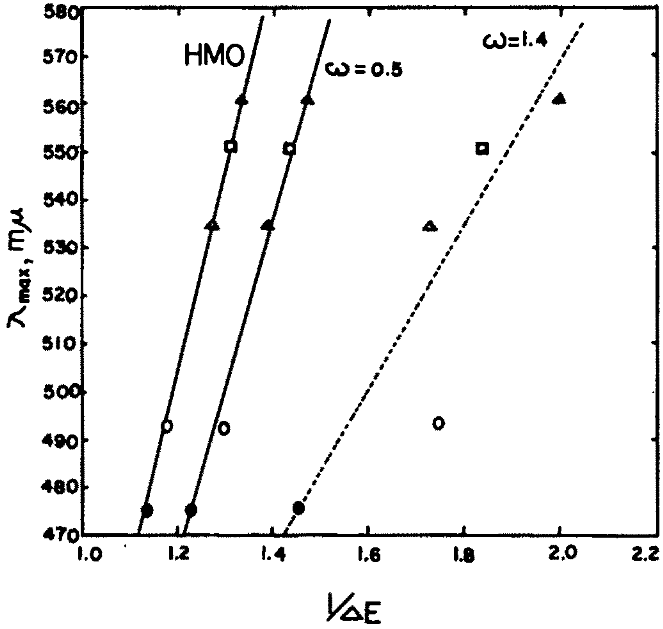

FIG. 4 Correlation of the lowest π–π^* singlet transition energies (ΔE in unit of x, $x = \alpha - E/\beta$) with the observed wavelength maxima (ordinate). ●: compound I, ○: II, △: III, □: IV, ▲: V.

Table 5 contains the calculated $\pi \rightarrow \pi^*$ singlet transition energies from the PPP MO, which generally yields reasonable spectral quantities. The assignments of the wavelengths were made on the basis of (1) energetically favorable orbital jumps and (2) calculated transition moments and oscillator strengths. The results agree quite well with the observed spectra in ethanol (0·1 % HCl).[2, 22, 23, 24] In the case of compounds I and II, there is excellent agreement. Even when the other compounds are assumed to be planar, they are qualitatively correct in that the compound calculated to have the longest wavelength does indeed show this experimentally. The calculated spectra of compounds III–V show better agreement, when the nonplanar conformations were assumed. Thus, it appears that the two rings in these molecules with —OH groups at position 3 are not coplanar in solution. Recently, a similar conformational problem was discussed in the case of biphenyl.[25, 26]

The only physical difference between all these compounds are the number and position of the OH groups on the molecule. These pigments have colors ranging from yellow to deep blues. Therefore, it must be the OH groups which determine this factor.[2] As the number of hydroxyl groups increases, the maximum wavelengths increase, and the colors go from yellow for I to purple for V. Also notice that by simply changing the position of one group, (e.g. II and III), the color changes from orange to red.

TABLE 5. THE $\pi \rightarrow \pi^*$ SINGLET TRANSITION ENERGIES CALCULATED BY THE PPP SCF ASMO CI METHOD

Compound	Color	Expt.		Calc.			
				Planar		Non-planar ($\theta = 45°$)	
I	yellow	2·607 eV	(476) mμ	2·607 eV	(476) mμ		
				3·146	(394)		
		4·541	(273)	4·829	(257)		
II	orange	2·515	(493)	2·549	(486)		
				2·959	(419)		
				4·182	(297)		
III	red	2·317	(535)	2·190	(588)	2·216 eV	(560) mμ
		2·850	(435)	2·904	(427)	3·027	(410)
		3·701	(335)	4·217	(294)	4·076	(304)
		4·592	(270)	5·276	(235)	4·334	(286)
IV	magneta	2·250	(551)	2·094	(592)	2·194	(565)
		2·818	(440)	2·890	(429)	2·908	(426)
		4·450	(278–9)	4·217	(294)	4·330	(286)
V	purple	2·210	(561)	2·087	(594)	2·179	(569)
		3·473	(357)	2·877	(431)	2·841	(436)
		4·492	(276)	4·290	(289)	4·378	(283)
VI				2·156	(575)		
				2·684	(462)		
				4·575	(271)		
VII	violet			2·034	(610)		
				2·505	(495)		
				4·504	(275)		

Compounds III–VII all have maxima longer than 500 mμ, while I and II are below this value. This apparently is due to the presence of the hydroxyl group at position 3. I and II are the only compounds without a OH group at this position. All these behaviors are reflected excellently by the PPP results in Table 5. Encouragingly, the simplest MO method does correlate reasonably, as shown in Fig. 4.

Fig. 5 shows the orientations of the calculated transition moments in the planar apigenidin molecule. It can be seen that the lowest transition (11 → 12) is polarized along the lateral axis of the molecule. The planar pelargonidin molecule (Fig. 6) has about the same features of the polarizations as in Fig. 5. The transition moment for the 12 → 14 transition has very small components along the x and y axes. Apparently, this particular transition is polarized mainly along the z axis, and the twisted conformation (Fig. 7) indicated this transition to be polarized along the perpendicular axis. It can be seen, from Fig. 7, that the twisting of the two ring

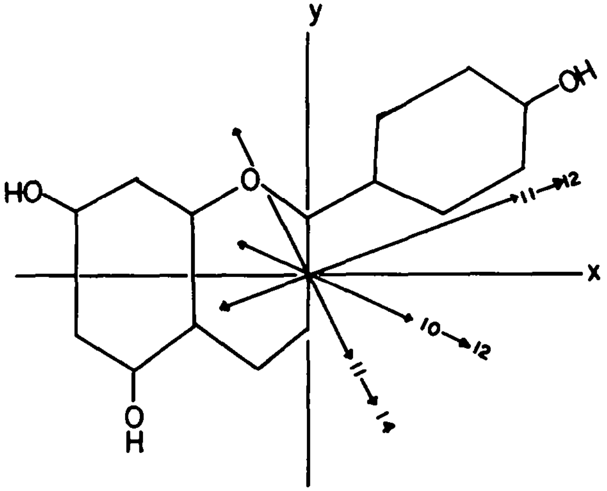

Fig. 5 The orientations of $\pi \to \pi^*$ transition moments in the apigenidin molecule calculated by the PPP SCF ASMO CI method.

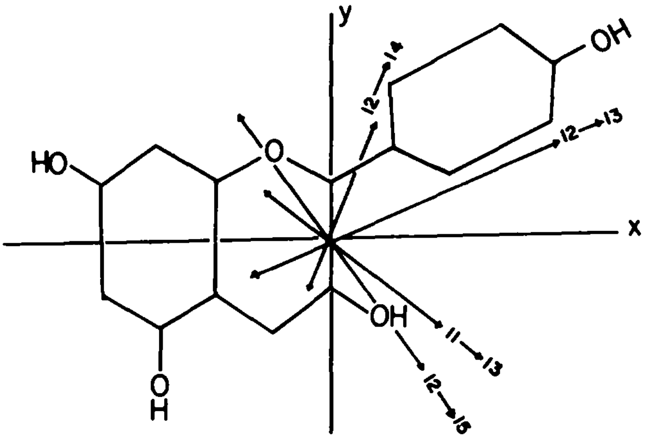

Fig. 6 The orientations of $\pi \to \pi^*$ transition moments in the pelargonidin molecule assuming the planar conformation.

systems by 45° does not affect the polarization significantly. Experimental polarization spectra of anthocyanidins are not available for comparison. Nevertheless, the theoretical predictions made in this section are of value in interpreting the spectral nature of the dye molecules.

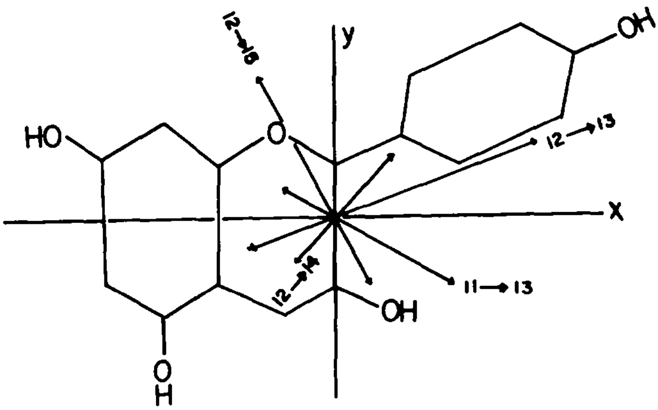

FIG. 7 The orientations of $\pi \rightarrow \pi^*$ transition moments in the pelargonidin molecule assuming a twisted conformation ($\theta = 45°$).

Table 6 shows the $\pi \rightarrow \pi^*$ triplet term values of the anthocyanidin molecules. The lowest triplets of apigenidin and luteolinidin are approximately at the 800 mμ region, while the others are at near IR or IR (for VI and VII) region. As expected, the twisting of the two rings raises the triplet levels. The triplet anthocyanidins may be of importance in their photochemistry. Anthocyanidins are involved in some photochemical processes.[27,28] The anthocyanidin formation is also intimately associated with the photoresponsive system of higher plants involving phytochromes.[29]

TABLE 6. THE $\pi \rightarrow \pi^*$ TRIPLET LEVELS (IN eV) CALCULATED BY THE PPP SCF ASMO CI METHOD

Compound	Lowest triplet		2nd triplet	
	Planar	Non-planar $\theta = 45°$	Planar	Non-planar $\theta = 45°$
I	1·530		2·354	
II	1·535		1·954	
III	0·836	0·850	2·074	2·289
IV	0·802	0·823	1·951	2·162
V	0·824	0·837	1·902	2·099
VI	0·294		1·501	
VII	0·264		1·347	

In conclusion, of the methods used in this study, we have seen that the HMO and ω-SCF methods appear to be qualitatively reasonable for predicting electronic properties of the ground state anthocyanidin molecules consistently. These methods are not especially good for excited state properties because of the lack of explicit electron correlations in the calculations. However, at least linear correlation between calculated λ_{max} and experimental spectra is found. Although the HMO is theoretically a more crude method than the ω-technique, it apparently often gives better results than the $\omega = 1{\cdot}4$ method. The PPP results agree very well with the observed spectral data. It was shown that some of the anthocyanidins may exist in the non-planar conformation in which the two rings are twisted by as much as or more than 45°. Results on two anthocyanidin anhydrobases are also presented, showing that the electronic properties and spectra of the neutral molecules are similar to the flavylium derivatives. Interestingly, in the plant the actual form of the flower dyes may be as a derivative of the anhydrobase.[30]

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APPENDIX

1. *Parameters for the HMO and ω-SCF HMO methods.* The Coulomb and resonance integrals were taken from Refs. 4 and 6. The convergence in the ω-calculations (both $\omega = 0{\cdot}5$ and $1{\cdot}4$) was obtained in 5–7 iterations using the set of parameters of Ref. 4. With the parameter set of Ref. 6 which has been compiled from various published sources, the convergence was obtained in 6 iterations for the $\omega = 0{\cdot}5$ calculations, but 12–20 iterations were required in the case of the $\omega = 1{\cdot}4$ calculations. The latter calculations yielded divergence for the calculations of luteolinidin, cyanidin, and delphinidin.

2. *Values of the integrals for the PPP method.* Values of the ionization potentials (I_p), the one-center electron repulsion integrals (rr/rr), and the core resonance integrals (β^{core}) are tabulated below.

Atom	I_p	(rr/rr)	bond	β^{core}
C	11·16 eV	11·13 eV	CC	−2·29 eV
O	26·14	18·82	CO	−1·95
O^+	34·95	19·65	CO^+	−2·29
=O	17·70	15·23	CO	−2·70

The value of β^{core} for the C_2—$C_{1'}$ bond was evaluated by the method of Gondo,[25] and the angle of 45° (θ) between the planes yielded −1·619 eV.