199. *Electronic Spectra of Conjugated Polyenes before and after Protonation.*

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Kuhn showed that the electronic spectra of molecules containing conjugated double bonds depend on an energy, V_0, indicating the relative importance of limiting resonance structures. In this paper V_0 for ten conjugated polyenes, before and after conversion into protonated mesomeric cations, are computed with the help of the light-absorption peaks. Numerical relationships of these V_0 values are discussed.

PREVIOUS papers [1,2,3] dealt with proton transfers of the type $A + B \rightleftharpoons C^+ \ldots D^-$, when A is trichloroacetic acid, B a conjugated polyene, and $C^+ \ldots D^-$ an ion-pair; the equilibrium constant is K, the dielectric constant of the solvent benzene and of the co-solvent A being too small to allow appreciable dissociation. The charge separation in $C^+ \ldots D^-$ could nevertheless be proved by electrical conductance measurements.

The electronic spectra of B and $C^+ \ldots D^-$ are different, but no attempt has been made to correlate the wavelength λ_1 of the light-absorption peaks with the structure of the protonated species. It is the purpose of this paper to do so by using a simple free-electron treatment developed by Kuhn.[4]

Calculation of V_0.—The π-electrons, responsible for the observed light-absorption peaks of B and $C^+ \ldots D^-$, are considered to be placed in a one-dimensional potential having a sine-curve periodicity along the chain of carbon atoms. The amplitude of the potential, V_0, a measure of the relative importance of the limiting resonance structures, can be calculated from

$$1/\lambda_1 = (V_0 - \boldsymbol{hc})(1 - 1/N) + (\boldsymbol{h}/8\boldsymbol{mc})(N + 1)/L^2 \quad . \quad . \quad . \quad . \quad (1)$$

where N is the number of π-electrons and L is the length of (Ångström units) the system of conjugated double bonds. The V_0 values of the following conjugated polyenes and of the corresponding protonated species are considered: ω-*p*-methoxyphenylpolyene-aldehydes, 5-phenylpenta-2 : 4-dienal, methylbixin, and vitamin-A acetate. On protonation mesomeric cations are obtained, which are represented by the limiting resonance structures (I)—(IV) respectively. The middle parts of the formulæ (III) and (IV) have been omitted because they are obvious from the known structure of the unprotonated polyenes.[5] The mesomeric cations (I), (II), and (III) are formed by protonation of a carbonyl-oxygen atom at the end of a system of conjugated double bonds. Protonation of a carbon atom is not considered in these cases, because of the greater electronegativity of oxygen. It could be suggested that the proton is taken up by the oxygen of the methoxy-groups in (I), but this is improbable.[2] Species (IV) is formed by " end-on " addition of a proton to a system of conjugated carbon–carbon double bonds. The evidence for this mode of reaction has been given,[3] and an alternative cation specified [3] which is formed by proton transfer to the carbon atom, indicated in (IV) by an asterisk. The chromophore lengths of (IV) and of the alternative mesomeric carbonium ion are identical. These proton transfers withdraw two π-electrons from the conjugated double bonds with formation of a hydroxy- or methylenic group, which does not participate in the conjugation. The protonation is thus treated as the proton transfer to an aromatic hydrocarbon.[6]

In dealing with mesomeric ions containing benzene rings, Kuhn [4] included only one side of the benzene ring in the chromophore, as indicated by the heavy lines in (I) and (II),

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[1] Wasserman, *J.*, 1958, 1014.

[2] *Idem, ibid.*, p. 3228.

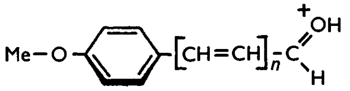
[3] *Idem, ibid.*, preceding paper.

[4] Kuhn, *J. Chem. Phys.*, 1949, **17**, 1198.

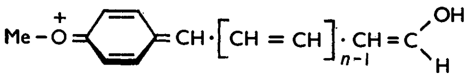
[5] Cf., for instance, Zechmeister, " Carotinoide," Springer, Berlin, 1934.

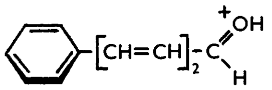
[6] See footnote 4 in ref. 3.

and in calculating chromophore lengths, L, he included one bond distance, l, beyond the terminal atoms forming the system of conjugated double bonds. We have adopted these conventions, all formal single and double bonds being taken as 1·46 and 1·34 Å respectively and l as 1·40 Å. The L value thus obtained was introduced into eqn. (1), together with the experimentally determined wavelengths, λ_1, and the appropriate number of π-electrons, N. The energy values, V_0, are listed in the Table. N, L, and V_0 of the protonated polyene aldehydes and of protonated methylbixin were also calculated on the assumption that the positive charge in one of the limiting resonance structures is not located on the carbonyl oxygen atom, but on the α-carbon atom. The results so obtained are not significantly different.

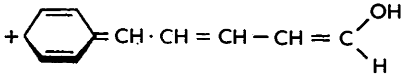


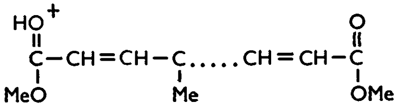
(I)



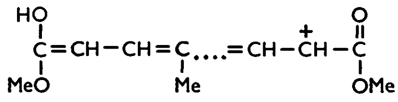


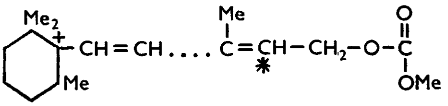
(II)



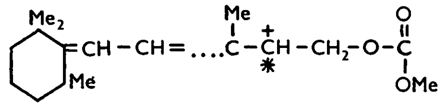


(III)





(IV)



V_0 *for conjugated polyenes before and after protonation.*

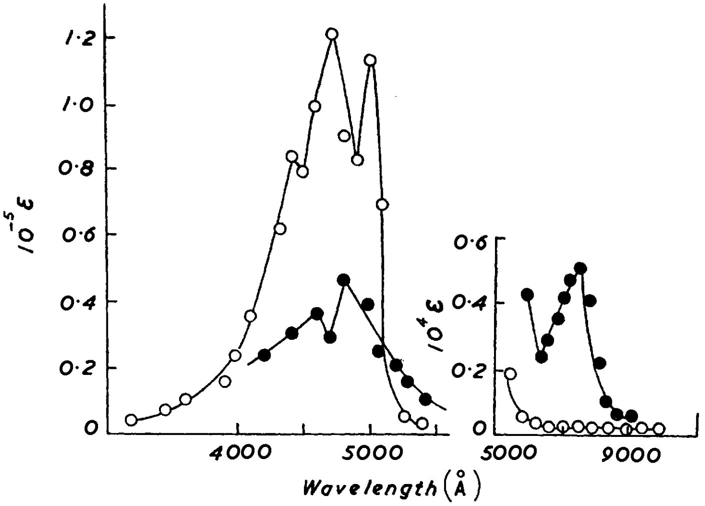
Proton donor: trichloroacetic acid; solvent: benzene; temp. ~20°.

		Before protonation			After protonation		
		λ_1 (Å)	N	V_0 (kcal./mole)	λ_1 (Å)	N	V_0 (kcal./mole)
ω-*p*-Methoxyphenyl-polyenealdehyde	$n = 1$	3200	8	55·2	3450	7	43·1
	$n = 2$	3500	10	52·5	3800	9	43·2
	$n = 3$	3700	12	50·6	4100	11	41·8
	$n = 4$	4000	14	48·9	4350	13	41·0
	$n = 5$	4200	16	48·0	4500	15	41·6
	$n = 6$	4400	18	46·4	4750	17	40·2
	$n = 7$	4550	20	44·7	4850	19	40·6
5-Phenylpenta-2 : 4-dienal		3200	9	53·5	3500	8	44·5
Methylbixin		4700	21	44·5	7500	20	17·7
Vitamin-A acetate ...		3300	9	57·1	6500	8	5·3

Discussion.—The V_0 values of the unprotonated and protonated ω-*p*-methoxyphenylpolyene aldehydes decrease, on the whole, with increasing n, indicating that in this homologous series, as in that previously discussed,[4] the relative contribution of one of the limiting resonance structures becomes less important if the number of conjugated double bonds is increased. Protonation produces in all cases a decrease of V_0, the variations in V_0 being smaller for unprotonated polyenes than for the protonated mesomeric cations. Thus the V_0 values in the top eight rows (right-hand column) are considerably larger than those in the last two rows of the Table; it is concluded that one of the limiting resonance structures predominates to a considerable extent in the mesomeric cations derived from the polyene aldehydes. This can be explained by a certain " localisation " of the positive charge near the electronegative carbonyl-oxygen atom. Methylbixin, in contrast to the polyene aldehydes, contains a carbonyl oxygen at both ends of its system of conjugated double bonds and, therefore, an effect due to unsymmetrical charge localisation could be less pronounced. The V_0 value relating to protonated methylbixin is, indeed, smaller than the values in the first eight rows of the Table. The smallest V_0 value, however, is that of the protonated vitamin-A acetate. In this mesomeric carbonium ion the positive charge appears to be more evenly distributed over the chromophore than in any of the other species here considered.

Experimental.—The λ_1 values in Table 2, except those of methylbixin, were taken from previous papers.[1,2,3] The light absorption of methylbixin, m. p. 163°, recrystallised from ethanol–chloroform, before and after protonation is in the Figure. The equilibrium coefficient K relating to the proton transfer from trichloroacetic acid to methylbixin [1,7] is $0{\cdot}4 \pm 0{\cdot}1$ l./mole in benzene solution at about 20°. The equilibrium measurements make it probable that one proton only is taken up. Experiments with dioxan [1,7] showed that the protonation is reversible. For methylbixin, $-\log_{10} \Lambda$ (l. mole^{-1} ohm^{-1} cm.$^{-1}$) is 7·08 and 6·26 when $-\log_{10} c$ [where c is the concentration of the ion pair $C^+ \ldots D^-$ (mole l.$^{-1}$) calculated from stoicheiometric concentrations and results of equilibrium measurements] is 2·72 and 3·69 respectively, at 25·0° in benzene.

Light absorption of methylbixin in benzene at 20°.



○ without acid; ● solution 3·68M in trichloroacetic acid; methylbixin concentration $1{\cdot}00 \times 10^{-4}$ to $6{\cdot}28 \times 10^{-4}$M.

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[7] Wassermann, *J.*, 1954, 4329.