A ``Metallic'' Model for the Spectra of Conjugated Polyenes

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(Received October 26, 1947)

The π-electrons belonging to the double bonds of *trans*-conjugated polyenes are assumed to be a one-dimensional electron gas in a field of uniform potential energy whose length is approximately that of the conjugated system. The energy levels, the selection rule (Δn odd) and the transition intensities are deduced. The model predicts that the oscillator strength of the main absorption band of a *trans*-conjugated polyene is given by $f = 0.134(2N+1)$, where N is the number of double bonds. The calculated values are in good agreement with experimental data. The wave number of the main band is related to the length of the conjugated system and the number of double bonds with moderately good agreement with experiment. The second, weaker absorption band of *trans*-carotene is discussed briefly.

INTRODUCTION

EVIDENCE has been accumulating that the π- or unsaturation electrons in organic molecules containing systems of conjugated double bonds have many of the characteristics of the "free" electrons in metals or semi-conductors. It is the purpose of this paper to describe the quantitative application of a simple "metallic" model to the electronic spectra of substances with relatively simple types of conjugated bond systems such as the *trans*-forms of the conjugated polyenes. A theoretical treatment of frequencies and intensities in the spectra of conjugated polyenes has been given by Mulliken[1] using the molecular orbital method in its LCAO approximation. The concept of quasi-classical electronic oscillators that was introduced by Lewis and Calvin[2] has been employed by Zechmeister *et al.*[3] to relate the spectra of the carotenoids to their constitution.

THE METALLIC MODEL

In the model to be discussed in this paper, the unsaturation electrons in the molecule of a conjugated polyene in its *trans*-form are considered to belong to the whole molecule and the usual approximations to the molecular orbitals are departed from by assuming the π-electrons to be

subject to a periodic potential field that is due to the chain of CH groups. The problem is regarded as analogous to that of the free electrons in the periodic field of a one-dimensional metal. The simplest approximation in the metallic case and one which is very valuable qualitatively if not so good quantitatively, is that of Sommerfeld[4] in which the electrons are regarded as a one-dimensional gas in a field of uniform potential. The same approximation will be adopted here, and it will be seen that it leads to results of much greater quantitative validity than might be expected in view of its obvious over-simplification.

Referring to Fig. 1, the x axis is chosen to coincide with the length of the conjugated bond system whose over-all length is X. If there are N double bonds in the conjugated system, there are $2N$ π-electrons that are considered to be a one-dimensional gas in a potential field which is uniform throughout the length X and which rises vertically to infinity at the ends of the system. The solution of the Schroedinger equation for this model[4] gives the energy levels (expressed as term values in cm^{-1})

$$E_n = \frac{h}{8mc}\frac{n^2}{X^2} = Bn^2/X^2$$
$$= 0.00302 \times 10^{-8} n^2/X^2, \tag{1}$$

where m is the mass of an electron, B represents the factor $h/8mc$, and n (the quantum number)

[1] (a) R. S. Mulliken, J. Chem. Phys. **7**, 364 (1939); (b) Rev. Mod. Phys. **14**, 265 (1942); (c) R. S. Mulliken and C. A. Rieke, Rep. Prog. Physics **8**, 231 (1941) for review and other references.
[2] G. N. Lewis and M. Calvin, Chem. Rev. **25**, 273 (1939).
[3] L. Zechmeister, A. L. Le Rosen, W. A. Schroeder, A. Polgár, and L. Pauling, J. Am. Chem. Soc. **65**, 1940 (1943).

[4] N. F. Mott and H. Jones, *Theory of Metals and Alloys* (Oxford University Press, 1936), pp. 51–53.
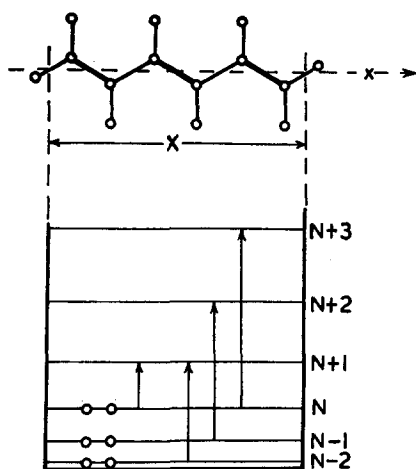
FIG. 1. Model of hexatriene (not accurately to scale) as typical of *trans*-polyenes, together with its energy diagram. The potential energy function is shown as a heavy line and the energy levels as light horizontal lines. The levels are filled up to N (which $=3$ in this case). Vertical arrows indicate the allowed optical transitions.

is an integer. The corresponding normalized wave functions are

$$\psi_n = (2/X)^{\frac{1}{2}} \sin(\pi n x/X). \qquad (2)$$

In the normal state of the molecule the $2N$ electrons, obeying Fermi-Dirac statistics, occupy the N levels of lowest energy, while the levels with $n \geqslant N+1$ are vacant.

The intensity of a transition between two levels whose quantum numbers are n and m is obtained in terms of the dipole strength D by

$$D = Q^2; \quad \text{where} \quad Q = \int_0^X \psi_n x \psi_m dx. \qquad (3)$$

The substitution $\theta = \pi x/X$ in the expressions for ψ_n and ψ_m gives

$$Q = (2X/\pi^2) \int_0^\pi \sin n\theta \cdot \theta \sin m\theta d\theta, \qquad (4)$$

and it is readily shown that the integral in Eq. (4) is zero if $(m-n)$ is *even*, while if $(m-n)$ is *odd*,

$$Q = (2X/\pi^2)[1/(m+n)^2 - 1/(m-n)^2]. \qquad (5)$$

The model thus leads to the *selection rule* that the spectrum contains only those transitions for which Δn is odd,[5] and in these cases Eq. (5) makes it possible to compute the intensities.

[5] This selection rule for the quasi-classical electronic oscillator was pointed out by Zechmeister *et al.* (reference 3).

The absorption spectrum will arise from allowed transitions from occupied to vacant energy levels. The transition of lowest energy is between the levels N and $N+1$, and the wave number of the band is

$$\nu(N, N+1) = (B/X^2)(2N+1), \qquad (6)$$

while its intensity in terms of Q is

$$Q(N, N+1) = (2X/\pi^2)[1/(2N+1)^2 - 1] \qquad (7)$$

or

$$|Q|(N, N+1) \approx 2X/\pi^2.* \qquad (7')$$

The transitions with next lowest energy are those denoted by $(N-2, N+1)$, $(N-1, N+2)$, and $(N, N+3)$, with $\Delta n = 3$ in each case (see Fig. 1). The wave numbers are given by

$$\left. \begin{array}{l} \nu(N-2, N+1) = (B/X^2)(6N-3) \\ \nu(N-1, N+2) = (B/X^2)(6N+3) \\ \nu(N, N+3) = (B/X^2)(6N+9) \end{array} \right\} \qquad (8)$$

and the intensity of each in all physically important cases can be approximated by

$$|Q| \approx 2X/9\pi^2. \qquad (9)$$

Intensity data relating to absorption bands are often quoted in terms of the oscillator strength f, which has been shown by Mulliken and Rieke[1c] to be given by

$$f = 1.08 \times 10^{11} \nu D = 1.08 \times 10^{11} \nu Q^2. \qquad (10)$$

Using the values of ν and Q from Eqs. (6) and (7'), the oscillator strength of the $(N, N+1)$ band is given by

$$\begin{aligned} f(N, N+1) &\approx 1.08 \times 10^{11} (4B/\pi^4)(2N+1) \\ &\approx 0.134(2N+1), \end{aligned} \qquad (11)$$

a relation that is important because it is independent of X, and depends only on N, the number of double bonds in the conjugated system. Regarding the $(N-1, N+2)$ band as representative of the three bands of about equal strength for which $\Delta n = 3$, we find from Eqs. (8), (9), and (10)

$$f(N-1, N+2) \approx 0.0050(2N+1). \qquad (12)$$

* The sign of Q is immaterial since it enters the expression for the intensity as Q^2.

COMPARISON WITH EXPERIMENTAL DATA ON *TRANS*-POLYENES

The main absorption band.—In comparing the predictions from this model with experimental data, it must be remembered that the predicted intensities expressed as oscillator strengths (Eqs. (11) and (12)) involve no empirical factors whatever except the arbitrariness that is implied in the original choice of the model. The predicted wave numbers (Eqs. (6) and (8)), on the other hand, are very sensitive to the choice of the value of X, the over-all length of the conjugated system. This point is illustrated by the cases of butadiene and octatetraene, whose molecules are shown drawn to scale in Fig. 2. The bond distances and bond angles are those of Schomaker and Pauling[6] for butadiene, namely, $C-H = 1.06A$, $C-C = 1.46A$, $C=C = 1.35A$, $C-C=C$ angle $= 124°$. It is not clear from first principles whether the effective length X should be taken as approximating to the distance along the x axis between the end carbon nuclei (shown as X_C in Fig. 2) or whether a better choice would not approximate to the distance between the end hydrogen nuclei (X_H). A calculation from the geometry of the butadiene model shows that $X_C = 3.66A$ and $X_H = 5.50A$. If these values are used in Eq. (6), the predicted wave numbers are $\nu = 113,000$ cm^{-1} and $\nu = 49,900$ cm^{-1}, respectively. The experimental value for ν(max.) of the longest wavelength absorption band in butadiene vapor is 48,200 cm^{-1} as quoted by Mulliken[7] or 47,700
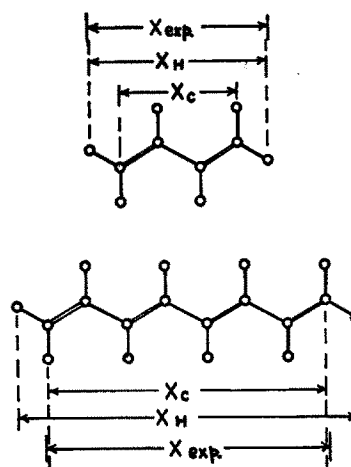

FIG. 2. Models of *trans*-butadiene and *trans*-octatetraene drawn to scale and showing relation between distances referred to in the text as X_C, X_H, and X_{exp}.

cm^{-1} according to Mulliken and Rieke.[1c] In this case it is clear that the choice of $X = X_H$ gives excellent agreement, whereas putting $X = X_C$ leads to a predicted value that is far from the truth.

In the case of octatetraene, using the bond distances and bond angles for butadiene, the geometry of the model gives $X_C = 8.62A$ and $X_H = 10.46A$, and the wave numbers calculated from Eq. (6) are 36,600 cm^{-1} and 24,800 cm^{-1}, respectively. Kovner[8] gives the experimental value of ν(max.) = 33,000 cm^{-1}, and in this case X_C is a good choice for the value of X, while X_H is a bad one. In the case of carotene, even the

TABLE I. Absorption bands of some conjugated *trans*-polyenes.

Substance	N	ν_{max} (observed) cm^{-1}	ν_{max} in gas (estimated) cm^{-1}	Length of conjugated system X in A		Oscillator strength f	
				X_{exp}	X_C	Experimental	Calc. by Eq. (11)
Butadiene	2	48000 (gas)[a]	48000	5.6	3.66	0.53[a]	0.67
Hexatriene	3	38500 (soln.)[b,c]	40500	7.2	6.14	(0.62)[e]	0.94
Octatetraene	4	33100 (soln.)[b]	35000	8.8	8.62	(1.55)[f]	1.21
Vitamin A	5	30750 (soln.)[d]	32700	10.1	11.10	1.05[g]	1.47
Carotene	11	22000 (soln.)[a]	24000	17.0	25.98	$\begin{cases} 2.69^a \\ 2.49^h \end{cases}$	3.08

[a] Mulliken and Rieke (reference 1c).
[b] Kovner, Acta Physicochimica **19**, 385 (1944), quoted by Maccoll, reference 8.
[c] Baly and Tuck, J. Chem. Soc. **93**, 1902 (1908).
[d] Zscheile and Henry, Ind. Eng. Chem. Anal. Ed. **14**, 422 (1942).
[e] Baly and Tuck (reference c above) show the absorption of hexatriene as being about the same strength as that of stilbene, for which $f = 0.62^a$.
[f] This is Mulliken and Rieke's semi-empirical value, reference 1c.
[g] Calculated from data of Zscheile and Henry (d).
[h] Calculated from data of Zechmeister *et al.*, reference 3.

[6] V. Schomaker and L. Pauling, J. Am. Chem. Soc. **61**, 1769 (1939).
[7] R. S. Mulliken, J. Chem. Phys. **7**, 121 (1939).
[8] M. Kovner, Acta Physicochimica **19**, 385 (1944), as quoted by Maccoll, reference 9.
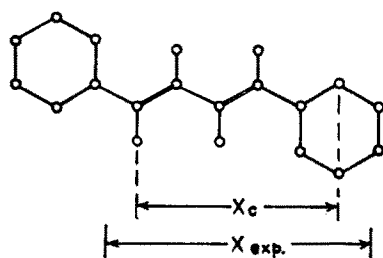
FIG. 3. Model of *trans*-diphenylbutadiene drawn to scale, showing relation between X_C and X_{exp} (H atoms attached to aromatic nuclei not shown).

choice of $X = X_C$ is too large, since it predicts $\nu = 10{,}300$ cm^{-1} in comparison with the experimental ν(max.) $= 22{,}000$ cm^{-1}. It is more instructive to use the experimental ν(max.) data to calculate the value of X which is required by Eq. (6) to give the best agreement with experiment. This value of X is denoted by X_{exp}, and is compared with X_C, which is chosen as a suitable length that is fixed by the geometry of the model. The data for the main absorption bands of five conjugated polyenes are collected in Table I. The values of X_C have been calculated on the assumption that the molecules are all *trans*, and that the bond distances and bond angles quoted above for butadiene apply throughout. Where the experimental ν(max.) were obtained in solution, they have been arbitrarily increased by 2000 cm^{-1} as a rough correction to the gas state.[1c]
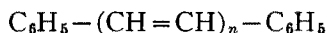
The series of diphenyl polyenes

$$C_6H_5 - (CH = CH)_n - C_6H_5$$

is one in which values of ν(max.) and f are available for all the members from $n = 0$ to $n = 7$. As representative of the series, Fig. 3 shows a model of *trans*-diphenylbutadiene drawn to scale assuming that the geometry of the polyene chain is the same as for butadiene (see above), while the distance $C - C$ (aromatic) is given its usual value of 1.39A. Reference to Table II shows that good agreement between the observed and calculated oscillator strengths of the bands over the whole series is obtained if the two terminal phenyl groups have the effect of contributing *one* double bond (i.e., two π-electrons) to the conjugated system. On this basis, the geometrical length X_C along the x axis between the end carbon nuclei of the effective conjugated system is as shown in Fig. 3. Table II compares X_{exp} and X_C and also the predicted and observed oscillator strengths. The experimental data are derived from Mulliken and Rieke[1c] and from Maccoll's summary[9] of the data of Hausser *et al.*[10] Hausser's ν(max.) values in benzene solution are consistently about 1500 cm^{-1} lower than Mulliken and Rieke's. The latter authors do not state what solvent was used; but it is known that the solvent displacement in benzene is usually greater than in non-aromatic solvents. The corrected ν(max.) for the gas state in Table II have been obtained by arbitrarily adding 2000 cm^{-1} to Mulliken and Rieke's ν(max.) values or 3500 cm^{-1} to Hausser's ν(max.). In any case the differences have little effect on X_{exp}.

Absorption bands at shorter wave-length.—In

TABLE II. Absorption bands of diphenylpolyenes $C_6H_5 - (CH = CH)_n - C_6H_5$.

n	Assumed value of N	ν(obs.) in solution cm^{-1}	Estimated ν in gas cm^{-1}	Length of conjugated system X in A		Oscillator strength f	
				X_{exp}	X_C	Experimental	Calc. by Eq. (11)
0	1	39700 41000[a]	43000	4.6	1.20	0.41 0.41[a]	0.40
1	2	31300 32000[a]	34000	6.7	3.68	0.58 0.62[a]	0.67
2	3	28400 30000[a]	32000	8.1	6.16	0.77 0.84[a]	0.94
3	4	26500	30000	9.5	8.64	1.26	1.21
4	5	24800 26000[a]	28000	10.9	11.12	1.39 1.42[a]	1.47
5	6	23600	27000	12.1	13.60	1.41	1.74
6	7	22500	26000	13.2	16.08	1.58	2.01
7	8	21500	25000	14.3	18.56	1.90	2.28

[a] Values from Mulliken and Rieke (reference 1c). All other experimental values are those quoted by Maccoll (reference 9).

[9] A. Maccoll, Quarterly Reviews 1, 16 (1947).
[10] K. W. Hausser, R. Kuhn, and A. Smakula, Zeits. f. physik. Chemie, **B29**, 384 (1935).

addition to the main absorption band, the model predicts a group of weaker bands (three bands if $N>2$) at roughly three times the frequency of the main band, and each with an oscillator strength about 1/27 that of the main band (Eqs. (8) and (9)). For the smaller conjugated polyenes this group would lie in the extreme ultraviolet and would be difficult to distinguish experimentally from Rydberg transitions. The model, which assumes the ionization energy to be infinite, will also begin to fail badly in the case of the lower members since the energy of levels such as $n = N+3$ will be of the order of magnitude of observed ionization energies. In the all *trans*-carotenes, however, the main band at about 22,000 cm^{-1} is accompanied by a much weaker band at about 35,000 cm^{-1} which is tentatively identified as arising from a transition for which $\Delta n = 3$, even though the model is badly out in its prediction of the position of the band. By calculation from the published absorption curves of Zechmeister *et al.*[3] for all *trans*- γ-carotene and all *trans*-lycopene, using the formula[1c] for the oscillator strength

$$f = 4.20 \times 10^{-8} \times 2.303 \epsilon_{\max}. \Delta \nu / 22.4, \quad (13)$$

($\epsilon_{\max}$. being the molecular extinction coefficient at the maximum, and $\Delta \nu$ the half-width of the band), one obtains $f = 0.57$ for the second band in γ-carotene and $f = 0.65$ for lycopene. The theoretical prediction (Eq. (12)) is $f = 0.12$ in each case. The calculations on the experimental data are admittedly rough, but if the observed band contains the *three* transitions $(N-2, N+1)$, $(N-1, N+2)$, and $(N, N+3)$, the theoretical value would be $f = 0.36$ in more reasonable agreement with the experimental values.

DISCUSSION

The "metallic" model that has been described in the preceding paragraphs has the obvious weaknesses that are associated with the original simplifying assumptions of a uniform potential field and an infinite ionization energy. In spite of these weaknesses, the agreement between the theory and the experimental data is good, particularly in the case of band intensities. The calculated oscillator strengths in Tables I and II involve no empirical factors whatever, whereas
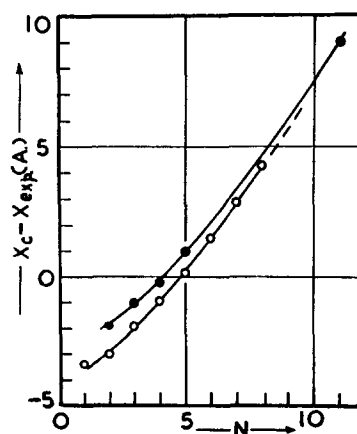

FIG. 4. Relation between $X_C - X_{\exp}$ in A, and N, the number of conjugated double bonds. Black circles—polyenes from Table I; open circles—diphenyl polyenes from Table II.

Mulliken and Rieke[1c] found that the usual LCAO approximations to the molecular orbitals required the introduction of an empirical correction factor of the order of magnitude 0.3 to reconcile theoretical and experimental f values. It has often been pointed out qualitatively that band intensities in the conjugated polyenes increase with the number of conjugated double bonds or with the length of the conjugated system,[1c,3] a relationship which is expressed accurately and quantitatively by Eq. (11).

The prediction of band frequencies is not as good, although even here the agreement with experiment is better than might be expected from the simplicity of the model. The length $X_{\exp}$. required to fit the experimental data to Eq. (6) is close to the geometrical length of the conjugated system when $N = 3$, 4, or 5, and for all the compounds treated there is a regular empirical relationship between $X_{\exp}$. and the length of the conjugated system as shown in Fig. 4, where the difference $X_C - X_{\exp}$. is shown plotted against N, the number of double bonds.

In its present simple form, the model cannot easily be extended to give a quantitative treatment of the *cis*- and the cyclic polyenes, or of the effect of introducing substituent groups or hetero-atoms such as sulfur and nitrogen into the conjugated system. At the same time, a qualitative emphasis on the "semi-metallic" nature of the π-electrons may be useful in problems concerning conjugated systems. By

extending the analogy with the electron theory of semi-conductors, the introduction of a hetero-atom into the conjugated chain would provide "impurity" or "trapping" levels for the electrons, and this concept may have a bearing on the fluorescence of such moecules. Furthermore, a conjugated molecule in an excited state has the partly filled energy levels that are necessary for "metallic" electrical conduction along the con-jugated chain. If there is a mechanism for electron transfer between neighboring molecules, one has a basis for the treatment of the phenomenon of photo-conductivity in conjugated systems.[11]

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Thermodynamics of the System Benzene-Biphenyl

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The vapor pressure of benzene and the heat of dilution of benzene-biphenyl mixtures have been measured at 25°C. The results are shown to be in fair agreement with Guggenheim's formulae based on the lattice model, assuming that the biphenyl molecule occupies twice the volume of the benzene molecule, and that the coordation number of the lattice is between 6 and 12. No agreement can be obtained if the effect of the different sizes is neglected.

The experimental results of other authors are critically examined and shown to conform to the above picture.

1. INTRODUCTION

MANY attempts have been made to derive formulae for the thermodynamic properties of mixtures of substances with different molecular sizes. With one exception, these have all been based on the concept of the molecules of a liquid or solution occupying sites arranged in a lattice. The lattice is not supposed to be of macrocrystalline size, but it is assumed that the regions of regular structure are large enough to allow the effects of the discontinuities to be neglected. One method of attacking the problem is to calculate directly the number of ways in which polymer molecules can be laid down in a lattice;[1–9] the other method is to obtain an ex-pression for the number of configurations by Bethe's method[10–17] or to establish the partition function directly.[18]

Guggenheim's formulae are the most rigorous and general; they include most of the others as special cases and reduce to those of Orr[14] for the case of a mixture of molecules occupying n sites and one site, respectively. Orr[19] has also carried out numerical calculations on certain special cases to establish the limits of accuracy of Bethe's method. Zimm[20] attempted to establish the thermodynamics of solutions of large molecules by applying J. E. Mayer's theory of condensing systems.

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