Physical Organic Chemistry

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John Wiley & Sons, Inc.

New York · London · Sydney

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Library of Congress Catalog Card Number: 63-20644
Printed in the United States of America

PHYSICAL ORGANIC CHEMISTRY

Preface

The field of physical organic chemistry may easily be considered to have originated with the publication of Hammett's classic text bearing that title. Much good work of this type had been done previously. However, the development of this field as one of major interest to organic chemists occurred in the mid 1940's after the publication of Hammett's book. More recently, several related works have appeared. The trend in these books has been to concentrate on the organic chemical aspects and to minimize the physical chemistry involved.

The present work represents an experiment in producing a useful text which would concentrate on the more physical chemical aspects. Since it was designed as a text rather than as a reference book, it has been necessary to select the topics considered with some care, and many interesting subjects and extensions of the subjects covered have been omitted in order to pare the mass of information which is available into an amount which could be covered in a reasonable length of time. My choice of subjects will undoubtedly not be universally agreeable. However, if the experiment proves to be a reasonable success, the experience gained by those who use this book will be a guide to future improvement.

The work is designed for a one-year graduate course, possibly in conjunction with a text which will present the more organic chemical aspects. The latter have been minimized herein because of the availability of texts emphasizing this aspect and because of a desire to minimize duplication of material.

The subject has been divided into three parts: Bonding and Spectra, Equilibria, and Kinetics. A considerable amount of integration has been possible so that material presented in one part is used as much as possible in a later part. The first sections of each part contain material which often will be covered in other courses. This material is included mainly as a review. Throughout the work, specific examples have been considered so that the student may see how the material presented may be applied to the study of organic compounds. Problems and reading lists have also been provided for many sections in order to help the student in gaining a good understanding of the material.

The final section, the Appendix, contains a variety of material which is designed to be useful. It contains a review of matrix algebra, tables of constants and other numerical data, and discussions of the practical treatment of nuclear magnetic resonance data and of kinetic data for reactions having complex rate laws. The final section of the Appendix includes a discussion of computer programming, since this subject is becoming of increasing importance to organic chemists, and since computers are now becoming fairly generally available. This is followed by some examples of computer programs which may be of interest to organic chemists.

Finally, I must acknowledge the contributions of former teachers and colleagues who started and nurtured my interest in physical organic chemistry. I should like especially to recognize the contribution of those at the University of Washington from whom I learned much and from whom I "borrowed" many ideas on how to present this material. Much of the work was written in Karlsruhe, Germany, during tenure of J. S. Guggenheim and A. P. Sloan fellowships. I wish to thank these organizations for their assistance and Professor R. Criegee, also, for making facilities available at the Technische Hochschule in Karlsruhe.

KENNETH B. WIBERG

New Haven, Conn.
November 1963

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PART ONE

Bonding and Spectra

1-1 Introduction

Any consideration of the theoretical aspects of organic chemistry must begin with a discussion of the nature of covalent bonding. Ideas of bonding have always played a central role in the development of organic chemistry, and the greatest achievement of organic chemistry—the development of the structural theory—is a direct outgrowth of the early, qualitative attempts to find an explanation for the attractive forces between atoms.

A modern consideration of the nature of covalent bonding and other attractive forces cannot be made without using quantum chemistry as the frame of reference. In order to do this as expeditiously as possible, the following discussion will first consider the principal approximation methods which are available and then some applications of these methods to problems of interest to organic chemists.

It will also be seen that a quantitative treatment of bonding will lead directly to the energy levels of each state of bonding of a given molecule. Since the observed spectra of molecules are related to the transition from one of these energy states to another, the following treatment will also permit a consideration of the spectral properties of compounds.

1-2 The Wave Nature of the Electron

In many ways electrons exhibit wavelike properties. For example, electrons will be diffracted in much the same way as ordinary light, the main difference being in the wavelength and thus in the spacing in the grating required in order to observe an effect. With ordinary light, a grating ruled with 1 to 10 thousand lines per centimeter is satisfactory, but with an electron beam, because of its shorter wavelength, no ordinary grating is adequate, and a crystal with its small distance between nuclei is used in order to observe diffraction.[1]

Accepting the wave nature of an electron, we can first qualitatively consider the effects of restraint on a species of this type. Suppose the particle having wavelike character were contained inside a one-dimensional box (Fig. 1-1) (i.e., it is permitted to move only along the x axis for a distance a). In order for the electron to be in a stationary state (of which more will be said later), we must also assume that the wave starts and finishes at the ends of the box. Thus the first wave we may draw is one which begins and finishes at the ends of the box and has no nodes. The next wave would have one node, the third would have two nodes, and so on.

Since for a wave of a given amplitude the energy increases with increasing frequency, it is apparent that the wave having no nodes has the lowest energy, what with one node is of higher energy, and that the energy of the state increases as the number of nodes increases. As will be seen later, for a given system this is, in general, the relationship between the possible wave functions and the energies.

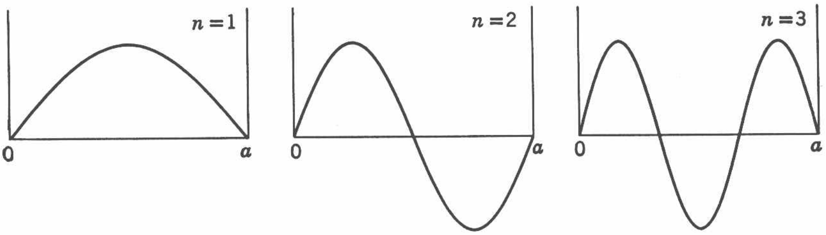

Fig. 1-1. Possible waves for a particle in a box.

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[1] For a review of the application of electron diffraction in studying molecular structure, see L. O. Brockway, *Revs. Modern Physics*, **8**, 231 (1936).

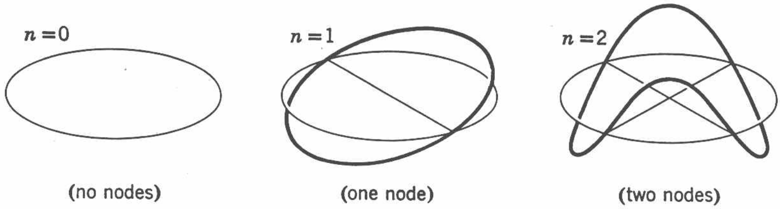

Fig. 1-2. Possible waves for a particle on a circle.

Another simple case is the particle on a circle. The particle is restrained to move along the circumference of the circle, and the waves corresponding to it are perpendicular to the plane of the circle. In order to obtain a stationary state the wave must return on itself, and therefore the possible wavelengths will be determined by the size of the circle. The first wave will have an infinite wavelength and no nodes, the second will have a nodal line bisecting the circle, and the next will have two nodal lines perpendicular to each other (Fig. 1-2). Again, the energy of a state will be a function of the number of nodes, that with no nodes having the lowest energy.

Reference

Development of Wave Mechanics:

J. C. Slater, *Quantum Theory of Atomic Structure*, McGraw-Hill Book Co., New York, 1960, vol. I, pp. 1–50.

1-3 The Postulatory Basis of Wave Mechanics

The preceding treatment will, of course, not give the energies of the possible states for these systems and cannot easily be extended to the more complex cases. Therefore we shall now examine the treatment of some of these cases by the use of wave mechanics. Certain postulates are fundamental to wave mechanics and have been developed by a consideration of the nature of the equations describing classical systems which are best considered as involving particles on the one hand and those considered as involving waves on the other. In a sense the postulates are not capable of direct proof, their validity being demonstrated by one's ability to calculate precisely the results of measurement by their use. The postulates may be stated in a number of possible ways. One way, which will be convenient for our purposes, is the following.

1. The fundamental equation of wave mechanics is

$$\alpha\psi = \lambda\psi$$

where α is an operator, ψ is the wave function or eigenpsi, and λ is the eigenvalue. The wave function is an expression describing the wave nature of the electron or other particle being considered, taking into account the restrictions imposed on it. The operator α simply does something to the wave function on which it operates. For example, the operation might be differentiation with respect to the coordinate, x. The nature of the operator to be used in a given problem will be discussed in more detail below. The eigenvalue λ is the value of the quantity corresponding to the nature of the operator used. Thus, for example, if one used the total energy operator, the value of λ would be the energy of the system.

2. For every dynamical quantity in classical physics, such as the distance, momentum, kinetic energy, and potential energy, there is a corresponding wave mechanical operator. In order to obtain the latter one writes the classical equation and replaces x by x and p (momentum) by $(-ih/2\pi)(\partial/\partial x)$. Thus the kinetic energy T is given by

$$T = \tfrac{1}{2}mv^2 = \frac{p^2}{2m} \qquad (\text{since } p = mv)$$

and the kinetic energy operator T_{op} is

$$T_{\text{op}} = \frac{p_{\text{op}}{}^2}{2m} = \frac{\left[\dfrac{-ih}{2\pi}\left(\dfrac{\partial}{\partial x}\right)\right]^2}{2m} = \frac{-h^2}{8\pi^2 m\left(\dfrac{\partial^2}{\partial x^2}\right)}$$

For a three-dimensional system, the latter is taken over all three coordinates.

3. For every state there is a corresponding wave function. The square of a wave function gives a probability. If a wave function is a description of the wavelike nature of a particle, then the square of the wave function should be analogous to an intensity (the square of the amplitude of a light wave gives the intensity of the light). The only meaningful concept of this type is the probability of finding the particle.

4. The only possible results of the measurement of a dynamical variable are the eigenvalues obtained from the wave equation. Thus there is an exact one-to-one correspondence between the values which are measured and those obtained from the wave equation.

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In order to have the wave functions correspond to physical reality, they must have certain properties. First, the integral of ψ^2 taken over all space must be finite:

$$\int_{-\infty}^{\infty} \psi^2 \, d\tau = \text{a finite value}$$

This follows from the statement that ψ^2 gives a probability. The integral then gives the total probability, which for a real case must be finite. Further, the wave function must be continuous and single valued. If this were not the case, then at some point in space there would be more than one value of the wave function and more than one value of the probability. This is impossible for any real case. These are the restrictions which make the wave function "well behaved."

1-4 Some Simple Examples

We can understand these postulates best by considering some simple examples. The simplest case we may treat is that of a free particle, which has only kinetic energy. Let us first obtain the possible results of a measurement of the momentum of the particle. We can write

$$p_{\text{op}}\psi = \bar{p}\psi$$

where p_{op} is the momentum operator and $\bar{p}$ represents the eigenvalues of the momentum. According to postulate 2, we replace p_{op} by $(-ih/2\pi)(\partial/\partial x)$ and obtain

$$-\frac{ih}{2\pi}\left(\frac{\partial\psi}{\partial x}\right) = \bar{p}\psi$$

The form of ψ must now be determined. It can be seen that in order to obtain a satisfactory wave function for this problem, the first derivative of ψ with respect to x must be equal a number times ψ. The type of function which will have this property is e^{ax} for

$$\frac{d}{dx} e^{ax} = ae^{ax}$$

It can be shown that for this case a is equal to $2\pi i/l$,[2] where l is the wavelength of the wave associated with the particle. Making this substitution, one obtains

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[2] K. S. Pitzer, *Quantum Chemistry*, Prentice-Hall, New York, 1953, p. 15.

$$-\frac{ih}{2\pi}\frac{\partial}{\partial x}e^{2\pi ix/l}=\bar{p}e^{2\pi ix/l}$$

$$-\frac{ih}{2\pi}\frac{2\pi i}{l}=\bar{p}$$

$$\frac{h}{l}=\bar{p}$$

This dependence of momentum on Plank's constant divided by the wavelength has been verified for a number of particles. In particular, electron diffraction experiments are a good test, for the momentum of the electron is a function only of the voltage used to accelerate it, and its wavelength may be determined from the spacings in the electron diffraction patterns of compounds whose crystal structure have been determined by X-ray studies. The above may be considered a partial justification for the nature of the wave function and operator which was used.

It should be noted that this result does not indicate any restrictions on the values of momentum which are allowed. This is the general result for all cases in which the particle is not bound (restricted to a certain portion of space).

We may now determine the results of a measurement of the energy of a free particle. The particle has only kinetic energy, and this is given by

$$T=\tfrac{1}{2}mv^2=\frac{p^2}{2m}$$

The wave equation is then

$$T_{\text{op}}\psi=E\psi$$

or

$$\frac{p_{\text{op}}^{\,2}}{2m}\psi=E\psi$$

where E is the value of the energy. Making the previously described substitution for p_{op}, we obtain

$$-\frac{h^2}{8m\pi^2}\frac{\partial^2\psi}{\partial x^2}=E\psi$$

The ψ used in determining the momentum will still apply here, and thus

$$-\frac{h^2}{8m\pi^2}\frac{\partial^2}{\partial x^2}e^{2\pi ix/l}=Ee^{2\pi ix/l}$$

Performing the indicated operation, we obtain

$$\frac{h^2}{2ml^2}=E$$

Here again the value of E is not quantized (restricted to certain definite values), but, rather, any values are possible, depending only on the wavelength of the particle.

We may now turn to two problems in which the particle is bound and in which we would expect to obtain a set of discrete energy levels. These are the particle in a box and the particle on a circle, the cases which were considered in a qualitative way in Section 1-2. For the particle in a box the wave function can be well behaved in the sense that it is single valued only if the wavelength l is related to the length of the box a by

$$l = \frac{2a}{n} \qquad n = 1, 2, 3, \ldots$$

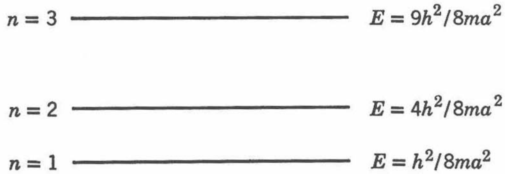
(cf. Fig. 1-1).[3] Introducing this value of l into the wave function used previously, we obtain

$$\psi = e^{i\pi x n/a}$$

The permissible energy levels are then obtained from

$$\begin{aligned} T_{\mathrm{op}}\psi &= E\psi \\ -\frac{h^2}{8m\pi^2}\frac{\partial^2}{\partial x^2}e^{i\pi x n/a} &= Ee^{i\pi x n/a} \\ \frac{h^2 n^2}{8ma^2} &= E \end{aligned}$$

Here we see that only certain values of energy are possible and that these are a function of the size of the box and of the quantum number n. The energy distribution is then



It may be noted that the energy required in going from one level to the next decreases as the size of the box increases. A simple molecular analogy to this case is a linear conjugated system. Here the box consists of the p orbitals which make up the π molecular orbital. Thus the length of the box is the length of the conjugated system. Consider the case of the polymethinium systems having m equal to 1, 2, 3, and 4.

$$(CH_3)_2N{-}(CH{=}CH)_m{-}CH{=}\overset{+}{N}(CH_3)_2$$

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[3] This may perhaps be more easily seen by writing the wave function of the energy operator in the equivalent form $\psi = \sin(2\pi x/l)$, where l is again the wavelength of the particle.

The spacing between the energy levels will vary with m because of the change in length of the conjugated system. The bond lengths are not known but may be taken as approximately 1.40 Å. Since alkyl groups are known to stabilize positive charges (cf. Section 1-15), the methyl groups probably contribute something to the length of the conjugated system, and this contribution was taken as approximately $\frac{1}{3}$ the C—C bond distance. Thus the values used were 6.53, 9.33, 12.13, and 14.93 Å for m equal to 1–4, respectively. The energy diagram for these conjugated systems calculated from the particle in a box approximation is given in Fig. 1-3. The x's represent the electrons in the conjugated system and are placed two to an energy level in accordance with the Pauli exclusion principle.

The lowest energy ultraviolet transition for these compounds would

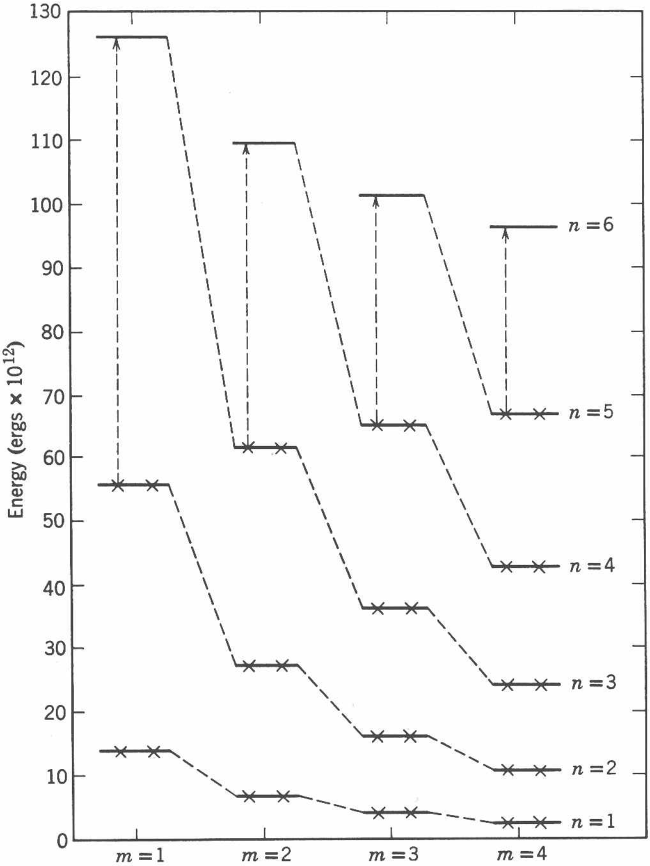

Fig. 1-3. Energy levels for some polymethinium ions.

correspond to the excitation of an electron from the highest filled level to the lowest unfilled level. This is shown by the vertical dotted lines in Fig. 1-3. The difference in energy may be converted to the frequency of the light which would be absorbed in causing this transition by the relationship $\Delta E = h\nu$, and the wavelength λ would be given by $\lambda = c/\nu$, where c is the velocity of light (3.00×10^{10} cm/sec). The calculated wavelengths and the corresponding observed values[4] are shown in Table 1-1. Considering the very simple approximation used, the agreement between the calculated and observed values is remarkably good.

Table 1-1 Spectra of Some Polymethinium Ions

m	*Calculated*	*Observed*
1	2830	3100 Å
2	4120	4120
3	5420	5100
4	6720	6600

A particle on a circle may be treated in the same way. In order for the wave function to be single valued and continuous, the wavelengths must be

$$l = \frac{2\pi r}{n} \qquad n = 0, 1, 2, \ldots$$

where r is the radius of the circle (cf. Fig. 1-2). Substitution into the wave function previously used gives

$$\psi = e^{ixn/r}$$

The wave equation is then

$$T_{\text{op}}\psi = E\psi$$

$$-\frac{h^2}{8m\pi^2}\frac{\partial^2}{\partial x^2}e^{ixn/r} = Ee^{ixn/r}$$

$$\frac{h^2n^2}{8\pi^2mr^2} = E$$

With the exception of the first energy level where $n = 0$ and $p = 0$, each of the energy levels may arise from either $+p$ or $-p$ as the momentum (corresponding to the particle moving around the circle in a clockwise or a counterclockwise direction). Thus for every value of n above the first there are two states with the same energy. They are referred to as degenerate states. The energy level distribution for a particle on a circle is then

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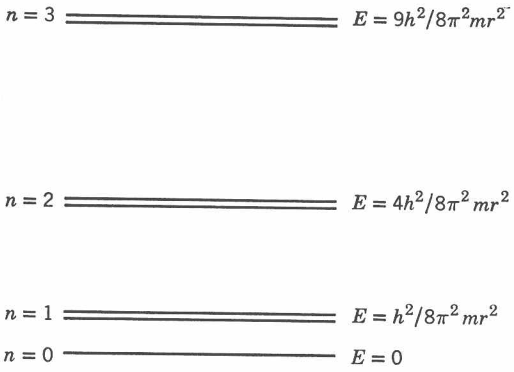
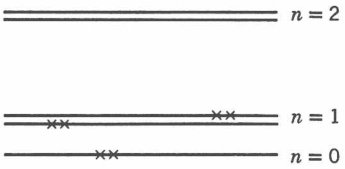
[4] H. J. Dauben, Jr. and G. Feniak, unpublished results.



Having this result, we may again look for a physical system which resembles this case and then try to apply the result as an approximation. A particularly good analogy is benzene, in which we may consider the electrons in a given energy level as being relatively free to travel in a circle of a radius equal to that of the ring. Again, placing two of the unsaturation electrons in each energy level, the distribution of these electrons in benzene would be



where the x's represent the electrons. A transition from the highest filled level ($n = 1$) to the lowest unfilled level ($n = 2$) would require the energy

$$\Delta E = \frac{(4 - 1)h^2}{8\pi^2mr^2}$$

Using the additional relationships, $\Delta E = h\nu$ and $\lambda = c/\nu$, the wavelength corresponding to this transition would be given by

$$\lambda = \frac{8\pi^2mr^2c}{3h}$$

If we make the appropriate substitutions ($h = 6.63 \times 10^{-27}$ erg-sec, $m = 9.04 \times 10^{-28}$ g, and $c = 3.00 \times 10^{10}$ cm/sec), this becomes

$$\lambda = 10.76 \times 10^{10}r^2$$

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