

THE THEORY OF RESONANCE

AND ITS APPLICATION TO
ORGANIC CHEMISTRY

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NEW YORK · JOHN WILEY AND SONS, INC.
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THIRD PRINTING, FEBRUARY, 1947

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE

The theory of resonance is the most important addition to chemical structural theory that has been made since the concept of the shared-electron bond was introduced by G. N. Lewis. Its general acceptance has doubtless been delayed to some extent, however, by the fact that, although the literature dealing with it has been voluminous, no comprehensive survey of the subject has existed. This book is intended to provide such a survey. It has grown out of a course of lectures which I have presented during the last several years to the advanced undergraduate and beginning graduate students at the University of Chicago. It has been written with the idea that its readers would have at least a sound knowledge of elementary organic chemistry, considerable familiarity with the electronic theory of valence, and some acquaintance with physical chemistry.

A comprehensive discussion of resonance offers difficulties. On the one hand, this theory has been found to have its most interesting applications, and to be of greatest value, in the field of organic chemistry. For that reason, it should preferably be presented in terms with which the organic chemists are familiar. On the other hand, its basis lies in the mathematical depths of quantum mechanics. For that reason, it can be presented precisely and completely only in highly mathematical language. Some sort of working compromise must therefore be reached. Since my own interest in the subject of resonance has been from the organic chemical viewpoint, it is inevitable that the final result should be heavily weighted in favor of the more qualitative and descriptive approach. Experience has shown, however, that often more difficulties are created than are avoided if the attempt is made to ignore entirely the underlying physical basis of the theory. Indeed, many of the present common misinterpretations of the theory seem to be directly attributable to the fact that practically all the discussions of it that have been published in the past (including, it must be admitted, some written by myself) have too drastically oversimplified the treatment. Consequently, a rather detailed, but non-technical and actually non-mathematical, discussion of the essential fundamental principles is given in Chapter 1, and particularly in Sections 1.5 and 1.6. No effort has been spared to make this discussion completely rigorous, even at the risk of

sometimes going into boring detail in regard to apparently trivial matters. Since the subject is unfortunately a very complex one, it cannot be adequately treated without a careful examination of a number of special cases, only a few of which may turn out to be interesting chemically.

I wish at this time to express my appreciation to Professor Linus Pauling, from whom I received my first and greatest inspiration to go deeply into the theory of resonance. This book is to be considered dedicated to him, in partial acknowledgment of my great indebtedness to him, even though the wartime restrictions on the use of paper have made impossible the inclusion of the customary dedication page.

I wish also to acknowledge the valuable assistance rendered me by the John Simon Guggenheim Memorial Foundation, which gave me the opportunity to develop some of the viewpoints and to gather some of the material used in this book; by Professors C. K. Ingold, J. E. Lennard-Jones, R. Robinson, and N. V. Sidgwick, who granted me the inestimable benefit of helpful discussions; by Professors H. C. Brown, R. S. Mulliken, F. H. Westheimer, and T. F. Young, and Doctors F. R. Mayo and V. Schomaker, who aided me by critically examining part or all of the manuscript; by Professors W. G. Brown and M. S. Kharasch, who permitted me to use an unpublished table of heats of combustion that they had compiled; and by Doctor D. F. Peppard, who helped me in reading proof.

Since it is hardly conceivable that this book could be completely free either of misprints or of errors in theory, interpretation, and fact, I would welcome any suggestions and corrections that the readers may care to make.

GEORGE WILLARD WHELAND

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Chapter 1

THE THEORY OF RESONANCE

1.1 The Structural Theory. Ever since the middle of the nineteenth century, the progress of chemistry, and especially of organic chemistry, has been closely associated with the development of the structural theory. One can, in fact, hardly question that this theory, more than any other single factor, must be given the credit for the remarkable advances that have occurred in the science during the last hundred years. However, in spite of its outstanding success in correlating and systematizing the vast body of facts with which it deals, its history has been marked from the very beginning by a series of attempts to revise and to amplify it in such a way that its field of usefulness might be extended still further.

A number of these attempts have met with complete acceptance, and now form an integral part of the theory. One thinks at once, in this connection, of the stereochemical ideas developed by van't Hoff and by Le Bel, of the concept of coordination developed by Werner, and of the electronic theory of valence developed by Kossel and by Lewis. To these must now apparently be added the theory of resonance, a description of which is the object of the present book.

Many of the features of the theory of resonance had already been anticipated by the organic chemists in their search for a more comprehensive structural theory. Early in the second half of the last century, it was found that for some substances, of which benzene was perhaps the most striking example, *no* completely satisfactory structures of the conventional type could be devised at all. The idea then slowly emerged that perhaps these substances must be described not in terms of one single structure but of two or even more structures simultaneously. At the outset, this idea was probably not essentially different from that denoted now by the word "tautomerism," as, for example, in Kekulé's theory¹ of "oscillation" in benzene. In time, however, a distinction came to be drawn. A vague suggestion of this new point of view is perhaps to be found as early as 1887 in the well-known centric structure of benzene.² Neither Armstrong nor Baeyer was very explicit about

¹ A. Kekulé, *Ann.*, **162**, 77 (1872).

² H. E. Armstrong, *Phil. Mag.*, [5] **23**, 73 (1887); *J. Chem. Soc.*, **51**, 258 (1887). A. Baeyer, *Ann.*, **245**, 103 (1888).

the exact significance of the centric bonds in this structure, but the idea was elaborated further by Claus³ (on the basis of his own, essentially equivalent, diagonal structure) so that it became surprisingly similar in some regards to that accepted now. A rather more definite suggestion appeared a few years later in Thiele's theory of partial valence,⁴ which was applicable not only to aromatic ring systems but also to open-chain unsaturated molecules.

1:2 The Theories of Intermediate Stages, Mesomerism, and Resonance. It was not until after 1920, however, that the ideas to be discussed in this and the succeeding chapters began to take precise form. The first important advances were made by two different groups of organic chemists, who came simultaneously and quite independently to very much the same final conclusions. On the one hand, Arndt and his co-workers in Germany brought forward the theory of intermediate stages (*Zwischenstufen*),⁵ and, on the other hand, various English chemists, of whom only Robinson and Ingold need be mentioned explicitly here, brought forward the theory of mesomerism.⁶ The significant feature which these theories had in common was that *they considered it possible for the true state of a molecule to be not identical with that represented by any single classical valence-bond structure, but to be intermediate between those represented by two or more different valence-bond structures.*

Since it is important that this new concept not be confused with tautomerism, let us discuss an example in some detail. We shall consider a molecule which is in an intermediate stage, or is mesomeric, between two structures. For definiteness, we can think of the substance in question as benzene. If this substance exists as a tautomeric mixture of molecules with the Kekulé structures I and II, then some of the molecules have structure I whereas the others have structure II, or, if the equilibrium is supposed to be mobile, any one molecule spends part of its time in structure I and the rest in structure II. On the other hand, if

³ A. Claus, *J. prakt. Chem.*, **37**, 455 (1888).

⁴ J. Thiele, *Ann.*, **306**, 87 (1899).

⁵ F. Arndt, E. Scholz, and P. Nachtwey, *Ber.*, **57**, 1903 (1924); F. Arndt, *Ber.*, **63**, 2963 (1930). Recently the adherents of this school have adopted the terminology of the English school. For a comprehensive survey of the subject, see B. Eistert, *Tautomerie und Mesomerie*, Ferdinand Enke, Stuttgart, 1938.

⁶ Since the theory in its present form is the result of a long and slow development, it seems desirable to give references here only to comparatively recent review articles. Of these may be mentioned especially: R. Robinson, *Two Lectures on an "Outline of an Electrochemical (Electronic) Theory of the Course of Organic Reactions,"* The Institute of Chemistry of Great Britain and Ireland, London, 1932; *J. Soc. Dyers Colourists, Jubilee Issue*, 65 (1934). C. K. Ingold, *J. Chem. Soc.*, 1120 (1933); *Chem. Rev.*, **15**, 225 (1934). The use of the word "mesomerism" is comparatively recent, having been proposed originally by Ingold in the former of the two papers mentioned above.

the substance is correctly described instead in terms of the theories of intermediate stages or mesomerism, the situation is quite different: All the molecules have the same structure; this structure, which does



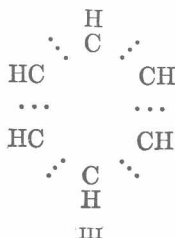
not change with the time, is not identical with either I or II, but it is intermediate between them.

Throughout this book, structures will be designated by Roman numerals. The first structure in each section will be assigned the number I.

The significance of the above distinction between tautomerism and the newer concepts can be made clearer with the aid of an analogy. A mule is a hybrid between a horse and a donkey. This does not mean that some mules are horses and the rest are donkeys, nor does it mean that a given mule is a horse part of the time and a donkey the rest of the time. Instead, it means that a mule is a new kind of animal, neither horse nor donkey, but intermediate between the two and partaking to some extent of the character of each. Similarly, the theories of intermediate stages and of mesomerism picture the benzene molecule as having a *hybrid* structure, not identical with either of the Kekulé structures, but intermediate between them.

In order to obtain a mental picture of such a hybrid structure, let us center our attention upon some particular bond, say the one between the two carbon atoms on the right sides of the structures I and II above. If benzene consists of a tautomeric mixture of molecules with the Kekulé structures, this bond is a double bond part of the time (structure I) and a single bond the rest of the time (structure II). On the other hand, if the substance is in an intermediate stage, or is mesomeric, between the Kekulé structures, the bond does not change with the time. Moreover, it is neither a double nor a single bond, but it is instead a new type of bond, not envisaged by the classical structural theory. We might call it a "one-and-a-half bond" (however, see Section 4-4) or possibly a "benzene bond." We can obtain a more definite picture by making use of the fact that the average density of electronic charge in the region between two carbon atoms is greater if the atoms are joined by a double bond than it is if they are joined by a single bond. Consequently, we can visualize the bond in benzene as one in which the density of charge is greater than would correspond to a single bond, but less than would correspond to a double bond.

The following difficulty arises in the minds of many people when they first encounter a discussion of the structure of benzene from the present point of view. The structures I and II are completely equivalent since either can be transformed into the other by merely a rotation of 60° in the plane of the paper. What then is the difference between these structures, and what is the meaning of the statement that the true structure of benzene is neither the one nor the other but something intermediate? Moreover, since the carbon atoms are in principle indistinguishable (unless they are of different isotopes), how can we say that a *given pair* of them are joined by a double bond in I and by a single bond in II? A partial answer to these questions has already been implied in the preceding paragraph; the statement that benzene is a hybrid of I and II means that the carbon-carbon bonds are not alternately single and double, as would be true if the molecule had either structure alone, but all are instead of the same, intermediate type. A deeper insight into the problem can be obtained from a more careful examination. Although the various carbon atoms are not distinguishable, the positions in space which they are capable of occupying *are* distinguishable. Consequently, we could define the difference between structures I and II by the statement that the "two easternmost atoms" are joined by a double bond in I and by a single bond in II. This statement has a definite meaning, even though the "two easternmost atoms" cannot be more precisely specified as being identical with, say, atoms 1 and 2, or 3 and 6, or the like. This interpretation is most logical if the molecule is considered to be held in a fixed orientation, as in a crystal lattice, but it is not actually restricted to any such special situation. A further way of evading the present difficulty is by considering a particular case in which two adjacent carbon atoms are distinguished from the remaining four either by being of a different isotope or by carrying different substituents. Then the difference between structures I and II is quite apparent, but the situation has been made too highly specialized to be completely illuminating.



A further question which occasionally arises is the following. If altogether eighteen electrons are employed in benzene to produce the six completely equivalent carbon-carbon bonds, then would it not be satisfactory and highly convenient to describe the bonds as three-electron bonds and to write the structure of the molecule simply as III? There are two different reasons why this proposed alternative is inferior to the method of description adopted in the preceding paragraphs. In the first place, the term "three-electron bond"

has already been defined to mean something quite different from the type of bond in benzene (see Section 2-5); and, in the second place, no corresponding description can be devised for the apparently very similar bonds in naphthalene and other condensed aromatic ring systems. Consequently, the use of the structure III for benzene would be not only confusing but also incapable of generalization to other closely related situations.

With the development of the quantum mechanics, it soon became apparent that the theories of intermediate stages and of mesomerism were not merely arbitrary hypotheses, as they had appeared to be when first advanced, but were two equivalent chemical expressions of what is known as quantum-mechanical resonance. This latter, more precise concept, which was reached first in 1926 by Heisenberg⁷ in quite another connection, is a simple mathematical consequence of the fundamental equations of quantum mechanics, and its essential correctness has been established beyond question. Its application to chemical problems was initiated largely by Pauling and his collaborators.⁸ This newer quantum-mechanical approach not only provides a sound theoretical basis for the earlier and less precise ideas outlined above but also supplements them in several important regards by introducing into them certain refinements or extensions which could have been reached in other ways only with greater difficulty. It leads, for example, to an understanding of the conditions under which a molecule can, or cannot, be expected to exist in an intermediate stage or mesomeric state, and, even more important, it accounts for the observed greater stability of those molecules of which mesomerism or resonance occurs. The first of these additional features of the more detailed theory will be discussed at some length in Section 1-4, and the second will be referred to at frequent intervals throughout the book, and especially in Chapters 2 and 3.

1-3 Nomenclature. As we have seen, the theory of intermediate stages, or of mesomerism, or, as we shall say hereafter, of resonance, is an outgrowth of several earlier and less precise theories. Perhaps largely on this account, the language used to describe it is unusually varied, and no single, uniform system of nomenclature has as yet been adopted for it. Thus, the fact that, in benzene, resonance occurs between the two Kekulé structures I and II of the preceding section can be expressed by the statements that the substance has a hybrid structure, that it is a resonance hybrid, that it is in an intermediate stage or mesomeric state, or that it resonates between the structures in question.

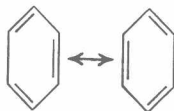
⁷ W. Heisenberg, *Z. Physik*, **38**, 411 (1926).

⁸ See L. Pauling, *The Nature of the Chemical Bond*, Cornell University Press, Ithaca, N. Y., 1st ed., 1939, 2nd ed., 1940, and numerous further references given there.

The structures themselves may also be said to resonate with each other, or to contribute to the state of the molecule. There is little to choose among these various equivalent modes of expression, and all can be used interchangeably.

Some authors speak of resonance between two, or among more than two, *forms*. This terminology is confusing, however, because the word "forms" commonly implies the actual existence of distinct substances which could (in principle, even if not always in practice) be separated from each other. Thus, we speak, for example, of the keto and enol *forms* of acetoacetic ester, the *d*- and *l*-*forms* of lactic acid, the rhombic and monoclinic *forms* of sulfur, and so on. The *structures* among which resonance occurs, however, are usually only intellectual constructions, which nevertheless are useful aids in the understanding of the true state of the molecule in question. This problem of the physical reality of the resonating structures is discussed in greater detail in Sections 1-5 and 1-6.

No unique symbols for the graphical representation of resonating molecules have as yet received unanimous acceptance. The most widely adopted procedure at present is a completely general, but rather cumbersome, one, which consists in writing down either all the structures involved or else a sufficient number of representative examples. The fact that resonance occurs among them is then indicated either by an explicit statement to that effect in the text or by the use of double-headed arrows,⁹ as in



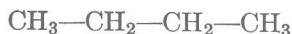
The symbol \leftrightarrow must, of course, be carefully distinguished from the similar one, \rightleftharpoons , which is commonly employed to show the existence of a chemical equilibrium. A further, more compact, system of representation, which was devised by the English school of organic chemists,⁶ will be described in Section 8-4.

1-4 The Conditions for Resonance. As was mentioned above, the quantum-mechanical approach leads to an understanding of the conditions that must be satisfied in order that resonance may occur. Although the following rules may perhaps seem arbitrary, since the reasons for them are not self-evident, it must be borne in mind that they, like the existence of resonance itself, are simple corollaries of the basic equations of quantum mechanics. In the present section, these rules will

⁹ C. R. Bury, *J. Am. Chem. Soc.*, **57**, 2115 (1935). B. Eistert, *Angew. Chem.*, **9**, 33 (1936).

be stated not quite rigorously, but in their simplest and most generally useful forms; in part D of Section 1-5, certain refinements in them will be discussed, which are required for complete rigor, but which almost never need to be considered explicitly in any practical application of the theory.

1. *Resonance can occur only between structures that correspond to the same, or to very nearly the same, relative positions of all the atomic nuclei.* Some such restriction as this is obviously necessary, since otherwise the phenomenon of isomerism would be impossible. If the two structures



I



II

I and II, for example, were able to resonate with each other, they could not represent two distinct and different substances, as they in fact do, but they would have to represent only a single substance with a structure of intermediate type. This last possibility, however, is precluded by the fact that the two structures in question correspond to widely different positions of the nuclei, so that the occurrence of resonance is rendered impossible by this condition 1.

The situation encountered generally in those molecules in which resonance does occur can be illustrated by a discussion of benzene. For this substance, the two Kekulé structures III and IV can be written.



III



IV

These do not correspond to exactly the same nuclear configuration because the length of a carbon-carbon single bond is normally about 1.54 Å, whereas that of a carbon-carbon double bond is normally about 1.34 Å. The symbol Å is an abbreviation for the *angstrom unit*, which is equal to 10^{-8} cm. (See Chapter 4.) However, atoms in molecules do not occupy definitely fixed positions; even at the absolute zero of temperature they are instead constantly executing vibrations about their positions of minimum potential energy with amplitudes of the order of magnitude of 0.1 Å. The above-cited lengths of single and double bonds refer only to the distances between these positions of minimum energy. Consequently, the two Kekulé structures do overlap in a sense, and so we need not be surprised if we find that resonance between them actually does occur.

A more detailed analysis of this first rule can be given with the aid of Figures 1-1, 1-2, and 1-3, which show in a schematic manner several possible ways in which the energy E of a given molecule may vary as the atomic positions change in consequence of a transition from some arbitrary structure R to a different structure S .

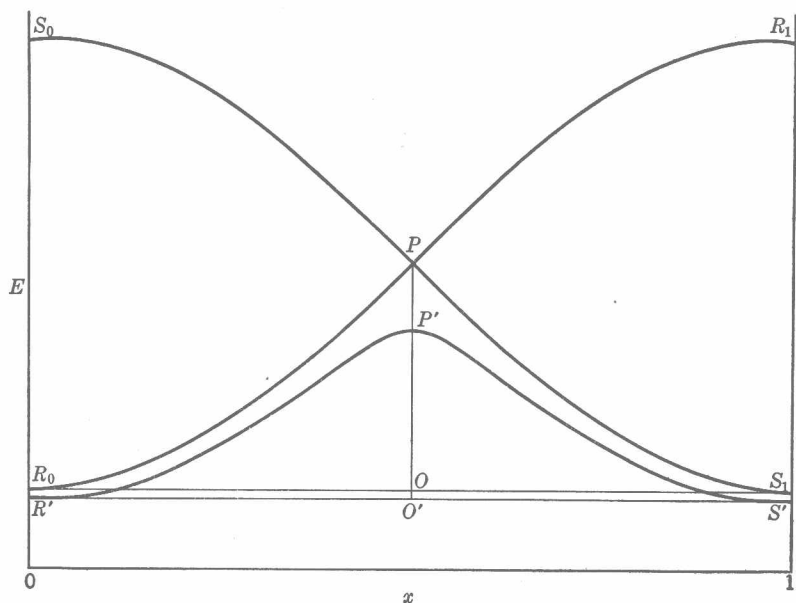


Fig. 1-1. Energies E of two structures R and S and of their resonance hybrid, when the limiting structures differ greatly in nuclear configuration. As the abscissa x varies from 0 to 1, the positions of the atoms change continuously from those characteristic of structure R to those characteristic of structure S .

The energy of a molecule is defined as the negative of the amount of energy required to dissociate it, in the gaseous state, into isolated gaseous atoms. The energy of a stable molecule is therefore always a negative quantity. In Figures 1-1, 1-2, and 1-3, the zeros from which the energies are measured would lie some distance above any of the curves. The word "stable," as used here and throughout the remainder of the book, indicates only a low energy and does not necessarily imply a lack of reactivity.

In each figure, the parameter x , plotted along the abscissa, is a coordinate which is described sufficiently for our purposes by the statement that it assumes the values 0 and 1 when the relative positions of the atomic nuclei are those corresponding to the structures R and S respectively, and that it assumes intermediate values when the atomic positions are intermediate. The energy of a molecule with structure R is

obviously a minimum at $x = 0$, since then by definition the molecule is in its most stable configuration, and it must increase along the curve R_0PR_1 as x increases, since in the process the molecule is being distorted from its stable configuration. Conversely, the energy of a molecule

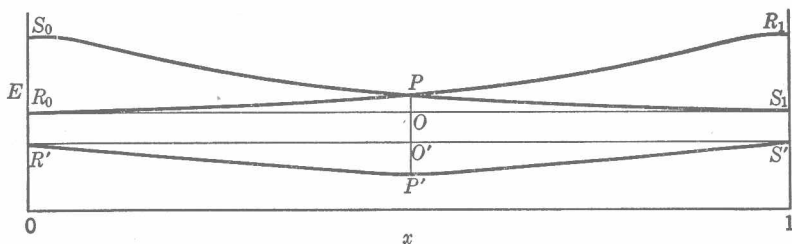


FIG. 1-2. Energies E of two structures R and S and of their resonance hybrid, when the limiting structures differ only slightly in nuclear configuration. The abscissa has the same significance here as in Fig. 1-1.

with the structure S has a high value (indicating instability) at $x = 0$, and must decrease along the curve S_0PS_1 to a minimum (indicating stability) at $x = 1$. For simplicity in exposition, the energies of structure R at $x = 0$ and of structure S at $x = 1$ have been assumed equal, and likewise the energies of structure R at $x = 1$ and of structure S at

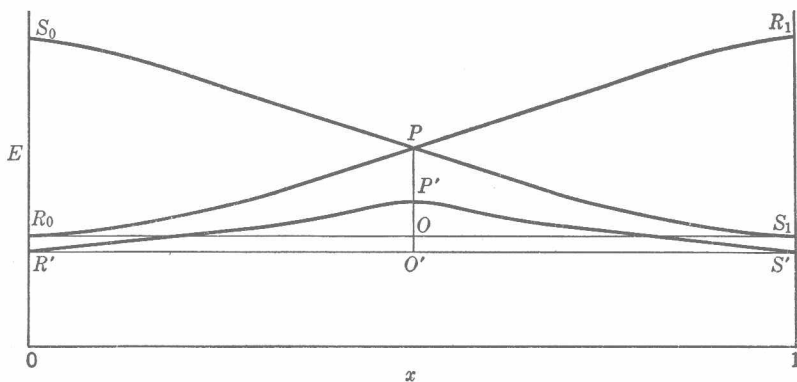


FIG. 1-3. Energies E of two structures R and S and of their resonance hybrid, when the limiting structures differ by an intermediate amount in nuclear configuration. The abscissa has the same significance here as in Fig. 1-1.

$x = 0$ have also been assumed equal; these assumptions are not essential to the following discussion, however, and the extension to the general case should be obvious.

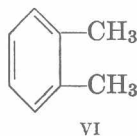
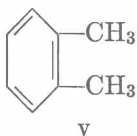
When the possibility of resonance between the structures R and S is taken into account, another factor arises. As has already been men-

tioned and as will be discussed later in greater detail (see, for example, Section 1.5 and Chapters 2 and 3), an important effect of resonance is to make a molecule in which it occurs more stable (that is, of lower energy) than any one of the individual structures involved. This is true, at any rate, of the most stable state of the system. The fact that resonance leads also to excited states in which there is an increase in energy has no bearing upon the present problem (see Section 1.5 and Chapter 6); we are discussing a chemical and not a spectroscopic question, and so we are concerned only with the most stable state, since that is the only state in which matter in bulk can be obtained. Thus, it follows that the actual energy of the molecule, when plotted against x , must give a curve $R'P'S'$, always below either R_0PR_1 or S_0PS_1 , but becoming nearly coincident with the lower of these at the extremes.

Figure 1.1 represents a case in which the structures R and S differ greatly in the relative positions of the atomic nuclei, so that a large distortion is required to change one configuration into the other. If resonance did not occur, the minimum energy necessary for the transition to occur would be represented in the figure by the distance OP ; when the resonance is taken into account, this energy is reduced to the smaller value $O'P'$. The distance OP , however, could easily correspond to an energy of 100 kcal per mole or more if the structures R and S differ in atomic configuration as greatly as do those of n - and i -butane, for example (structures I and II, respectively). Consequently, even when allowance is made for the resonance effect, the energy $O'P'$ required for the rearrangement may still be very large compared with the average thermal energy of the molecules. Under such circumstances, then, the isolation of isomeric or tautomeric forms possessing structures very close to R and S is possible, and it is not profitable to speak of resonance. (This point is discussed at greater length below in the paragraph in fine print.)

Figure 1.2 represents another extreme case, in which the difference in the atomic configurations of the structures R and S is relatively small. The energy of distortion OP is then also relatively small, being perhaps no greater in order of magnitude than the average thermal energy. If the resonance effect is assumed to be of about the same importance here as in the previous example, the curve $R'P'S'$ has no maximum but a minimum instead at some value of x intermediate between 0 and 1. Under such circumstances, the molecule will take up a configuration corresponding to this minimum. Isolation of isomeric or tautomeric forms possessing structures close to R and S will then be impossible; there will instead exist only a single substance, possessing a structure intermediate between R and S . This is the situation which one ordi-

narly has in mind when he says that a molecule resonates between two or more structures. In the particular case of benzene, only a single substance is possible whether resonance in this sense occurs or not (that is, whether the situation is that described by Figure 1-2 or by one of the others) because the two Kekulé structures III and IV are completely equivalent. With *o*-xylene, on the other hand, the two corresponding structures V and VI are not completely equivalent, and the possibility arises that two isomeric substances may exist. However, only one



o-xylene is known; it seems probable, therefore, that the relationship between V and VI (and also, from analogy, between III and IV) is that represented by Figure 1-2. Further evidence supporting this conclusion will be advanced in later chapters.

Figure 1-3 represents an intermediate case in which the curve $R'P'S'$ has a low maximum at the point P' . If the energy $O'P'$ is of the same order of magnitude as, or is smaller than, the average thermal energy, no isolation of isomeric forms will be possible. This situation is encountered, for example, in ammonia, NH_3 , in which the transition from one structure to the other occurs whenever the nitrogen atom passes through the plane defined by the three hydrogen atoms. In such borderline cases, which fortunately seem to be rather rare, the question whether one should speak of tautomerism or of resonance cannot be answered unambiguously without reference to some specific experimental situation. We shall return to this problem again in part D of Section 1-5.

Even in the situation represented by Figure 1-1, the points R' and S' lie slightly below R_0 and S_1 , respectively. In a certain sense, therefore, it might be said that resonance does occur between the two structures. This, however, is not at all what one ordinarily has in mind when he speaks of resonance. For example, let us suppose that the structures R and S are those given above as I and II respectively. (The small difference in energy between *n*- and *i*-butane is negligible for our present purposes.) Then, at $x = 0$, the relative positions of the atoms are those characteristic of *n*-butane, so that structure S should really be written not in the form II but rather in the form II', where the dotted lines represent the formal bonds discussed in part 3 of this section. (The structure II' is intended to imply that the electrons are shared as in *i*-butane, but that the geometrical arrangement of the atoms is as in *n*-butane.) In the same way, at $x = 1$, the structure R becomes I' instead of I. In other words, the resonance which can be said to occur between the structures of *n*-