

# THEORETICAL PRINCIPLES OF ORGANIC CHEMISTRY

by

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ELSEVIER PUBLISHING COMPANY

AMSTERDAM LONDON NEW YORK PRINCETON

1958

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(abbreviated)

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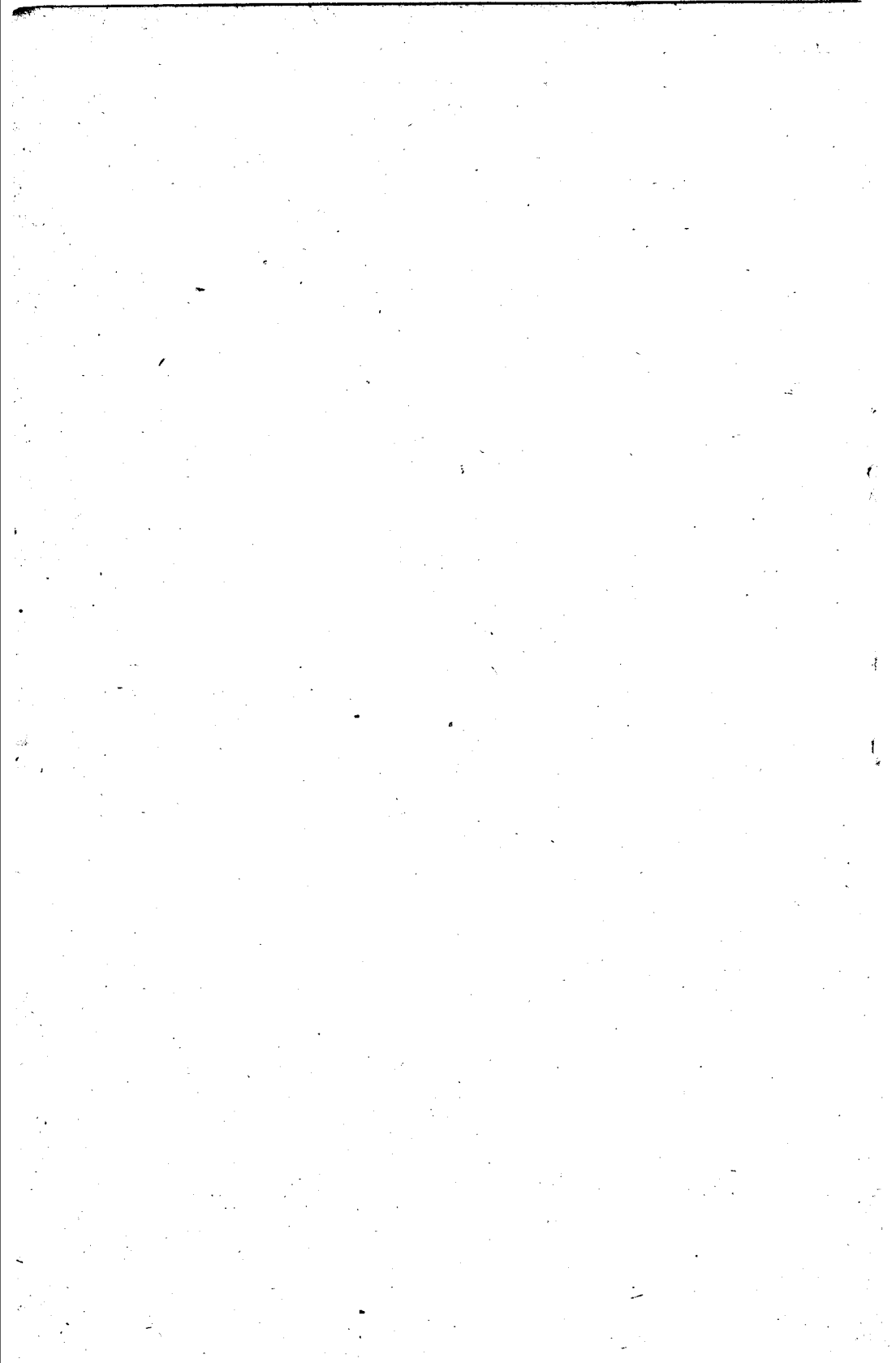
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**BOOK III**

**CONSTITUTION AND PHYSICAL PROPERTIES**



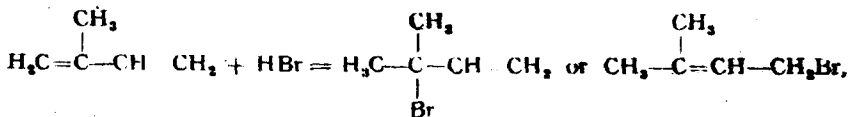
## CHAPTER XI

### THEORETICAL CONSIDERATION OF PHYSICAL PROPERTIES. THERMAL MAGNITUDES

#### (i) PHYSICAL PROPERTIES IN GENERAL

Chemical methods for the determination of constitution reach their limit where the principle of the least possible change in structure during chemical reactions is no longer applicable. Nevertheless, it is often possible, even in such cases, to hit upon the true structural formula by means of a critical consideration of the various methods that lead from one compound to another. Chemical methods do not, however, suffice to determine the kind or nature of finer differences in bonding type leading to characteristic differences in reactivity, as is evident in the case of transformation reactions in conjugated and aromatic systems.

Physical methods for the determination of constitution constitute a valuable extension to the chemical methods which always involve a greater or lesser attack on the structure of the molecule. In the case of physical methods the molecule of the compound investigated remains unchanged. The relationships valuable for the application of the physical methods are first obtained purely empirically by observation of the physical properties of compounds with a structure definitely determined by chemical methods. By this means an extensive mass of observational facts has been obtained. These data can then be used in determining the structures of compounds in such individual cases in which the chemical methods fail. This has been done frequently in the past; one need only recall the example of the determination of the constitution of the labile allyl halides (Vol. I, p. 394). In this case the chemical methods left undecided the question whether the addition of hydrogen bromide to isoprene led first directly to the tertiary or to the primary bromide:



as well as the constitution of the substance finally obtained. Application

of the observations made on the boiling points of the saturated, stable halides, according to which the tertiary halides boil at much lower temperatures than do the primary, while the boiling points of the bromides show a definite difference with respect to the boiling points of the structurally identical alcohols, led to a certain answer to this problem. In the same way the constitution of tautomeric compounds of the carbostyryl type could be determined by means of experimental measurements on light-absorption (Vol. I, p. 321), while in another case measurements on molecular refraction enabled a decision to be made between the open chain oxo-form and the cyclic semi-acetal form (Vol. I, p. 276).

Proofs of constitution made by such methods are however only proofs by analogy, the certainty of which is guaranteed by extensive factual data. Their power of conviction gains enormously when the fundamental relationships between constitution and physical properties can be given a theoretical interpretation. Such a theoretical interpretation and understanding is absolutely essential when we deal with questions of structure which cannot be decided uniquely by chemical methods, or when only a few cases of analogy are known.

We find such a necessity for deriving the constitution from the physical properties, for example, in the case of the determination of the configuration of the majority of the stereoisomeric ethylenes. The cases in which the configuration can be determined by chemical methods by means of the principle of intramolecular reactions of neighboring groups, or in which the configuration may be derived by relation to another configuration, and definitely established by such methods, are very rare indeed. Hence, from the scattered data on melting points, boiling points, densities, etc., of the relatively small number of compounds with a definitely established configuration, it is not possible to derive the configurations of other, often quite differently built, substances. Thus, for example, it is not permissible without further consideration to expect like-signed differences in the various physical properties of the maleic and the fumaric acid esters on the one hand, and the *cis*- and the *trans*-dichloroethylenes on the other hand. Only when one completely masters the theoretical relationships involved is one fully protected against deceiving conclusions drawn from analogy. From a purely empirical point of view one will quite frequently be led to contradictions, when drawing upon the most varied physical properties for purposes of comparison;—a large number of examples to illustrate this statement will be given later <sup>1</sup>.

<sup>1</sup> Compare for example the "determination of configuration" of the dimethylsuccinic acids as based upon their melting points, and as already discussed in Vol. I, p. 341, footnote 139.

A very important group of problems, in the solution of which organic chemistry and physics as well are equally interested, consists then in the theoretical grasp of the relationships between constitution and physical properties. While knowledge in this field has not as yet advanced very far, one can at least see the ways in which progress can be made. Heretofore the relationships between constitution and physical properties of organic compounds have been treated essentially from the practical point of view, *i.e.* of determining the constitution. While in what follows this point of view should give way more and more to the theoretical viewpoint, it will, as the simpler one, be described briefly at first <sup>2</sup>.

### (a) Additive Properties

One group of properties of particular practical use in structure-determinations is that known collectively as the group of "*additive properties*" <sup>3</sup>. The numerical values of the magnitudes taken as a measure of such properties can be represented as a sum of individual values characteristic of the atomic species present in the various compounds. The "mass" may be considered as a *strictly additive* property, made up of the sum of the masses of the individual atoms to within the *limits* of the greatest *experimental accuracy* achieved thus far <sup>4</sup>, independently of type of bonding in which the atoms exist <sup>5</sup>. Thus for all compounds the molecular weight, *i.e.* the sum of the atomic weights, is a strictly additive property. Being thus completely independent of the constitution, it can of course not be used in problems of structure-determination. If a property is to be used for this purpose it must be such a one as shows definitely regular, constitutively peculiar, deviations from additivity; as for example when a double or triple bond between atoms replaces a single bond, as in the case of three  $C_6H_{12}$  isomers, cyclohexane and hexene. The properties of the substance must then depend not only on the nature of the atoms present in the molecules, but also on the state of the bonds holding them together.

The numerical value of such more generally additive properties may then be composed of a sum of those values characteristic of the atoms themselves, independent of their states of union with other atoms or groups, together with values characteristic of the particular bonding states. As an illuminating

<sup>2</sup> For a detailed monograph see: R. KREMAN, *Zusammenhänge zwischen physikalischen Eigenschaften und chemischer Konstitution* (Relations between physical properties and chemical constitution), in *Wissenschaftl. Forschungsberichte*, Vol. 41 (Th. Steinkopff, Leipzig and Dresden, 1937).

<sup>3</sup> W. OSTWALD, *Allgemeine Chemie*, 2nd edition, p. 1121 (1891).

<sup>4</sup> H. LANDOLT, *Abhandl. Bunsen-Ges.*, (1908) No. 1.

<sup>5</sup> Theoretically this is of course contrary to the mass energy relation,  $E = mc^2$ .

example we may cite the case of the heats of combustion of the isomers of cyclohexane and of hexene named above. In the case of aliphatic hydrocarbon compounds, the heat of combustion is, to a first approximation, an additive property; isomers with the same atomic bonding states, but with different structures, have approximately the same heats of combustion; the presence of several multiple bonds produces regular deviations from this additivity. One may *think* of the combustion process as composed of several stages:—that, first of all, all the bonds are broken by application of energy, and that then the individual atoms are oxidized with evolution of energy. The heat of combustion of a single carbon or hydrogen atom is always the same, regardless of the bonding state in which it had previously existed. The difference in the heats of combustion of cyclohexane and hexene is then due only to the different states of bonding; in cyclohexane it is necessary to break 12 C—H- and 6 simple C—C-bonds; in the case of hexene, however, 12 C—H- and 4 simple C—C-bonds, as well as 1 C=C-double bond. The observed value of the heat of combustion is thus composed of the sum of the heats of combustion characteristic of the free atoms minus the (thermal equivalent of the) work of breaking the molecular bonds. Without new, independent aids, which in the preceding example would have to lead to the heats of combustion of atomic hydrogen and atomic carbon, it is impossible to separate from one another the two effects,—of the kinds of atoms and the types of bonding. While such a separation must seem very important from a theoretical viewpoint, just so unimportant is it from a practical viewpoint. For in a compound one can just as well count up together the similar types of atoms as the similar types of bonds; the numbers thus obtained are related to one another by functions determined by the valences of the atoms. One may, therefore, carry out the calculations as if the observed values of the properties depended either only upon the atoms or only upon the types of the bonds. Depending then upon the manner of subdivision used, one obtains the so-called atomic or the so-called bonding constants, through the summation of which the value of the property of any and every compound desired may be calculated. It is usual to use atomic constants. With them the value of a property  $E$  is expressed as follows:

$$E = m \cdot c + l \cdot h + p \cdot o + q \cdot n + \dots\dots\dots$$

where  $c, h, o, n, \dots$  etc. denote the atomic constants of the elements C, H, O, N, etc., and  $m, l, p, q, \dots$  etc., the numbers of atoms of each of these present in the compound in question. Using the bonding constants, the corresponding summation is given by:

$$E = x(c \dots c) + y(c \dots h) + z(c \dots o) + r(o \dots h) + s(c \dots n) + \dots\dots\dots$$

where  $c \dots c, c \dots h, c \dots o, o \dots h, c \dots n$ , etc. represent the bonding constants for C—C, C—H, C—O, O—H, C—N... etc., and  $x, y, z, r, s, \dots$  are the numbers of the corresponding bonds present in the given compound.

The atomic or bonding constants in practical use are then primarily magnitudes to which a theoretical significance cannot always readily be given. For in the usual method of resolution used, the atomic constants contain terms that really depend on the state of bonding. If instead we use bond constants, these in turn contain terms that depend really on the atoms, independently of the state of bonding. This follows directly from the manner of calculating the constants. The atomic constants are obtained by the following method or scheme of calculation, in which  $a$  and  $b$  in each case denote the measured values of the physical magnitudes momentarily under consideration. Thus for the compounds  $C_2H_6$  and  $CH_4$  we have:

$$\begin{array}{rcl} \frac{C_2H_6 \dots a}{-(CH_4 \dots b)} & \frac{CH_4 \dots b}{-(CH_4 \dots a-b)} & \frac{CH_4 \dots a-b}{-(h_2 \dots 2b-a)} \\ \hline ch_2 = a - b & h_2 = 2b - a & c = 2a - 3b \end{array}$$

$$h = b - \frac{a}{2}$$

For the bonding constants we have the following derivation:  $CH_4$  has 4 C—H-bonds. If the measured value of the physical magnitude  $b$  be divided equally over these four bonds, then the value ( $c \dots h$ ) for a single C—H-bond is given by

$$(c \dots h) = \frac{b}{4}$$

$C_2H_6$  has 6 C—H-bonds and 1 C—C-bond. The value of  $a$  measured for  $C_2H_6$  must be subdivided for these bonds; the part corresponding to the C—H-bonds is deducted, and the remainder is the bonding constant for the C—C-bond:

$$c \dots c = a - \frac{3}{2}b$$

From a purely calculational point of view, we have then, on the basis of the method applied, the following relations:

$$\begin{aligned} c &= 2(c \dots c), \quad 2h = 2(c \dots h) - (c \dots c), \\ (c \dots c) &= \frac{1}{2}c, \quad (c \dots h) = \frac{c}{4} + h, \end{aligned}$$

where of course the terms ( $c \dots c$ ) etc. are unit terms, not algebraic differences.

The calculation of the atomic constants  $2h$  then includes the values of the properties determined only by the states of bonding, in particular of the bonding value of the C—H-bond multiplied by the factor 2, and of the C—C-bond with the factor —1. Conversely, the calculation of the bonding constant ( $c \cdots h$ ) includes values due to the atoms above, in particular the values of  $c$  and  $h$  with the factors  $1/4$  and 1, respectively.

These calculations thus show, among other things, the nature of the atomic and bonding constants in (general) practical use as calculational magnitudes without any direct physical significance. Hence these numerical values of the usual constants cannot be used as a starting point for theoretical considerations until the "atomic" and the "constitutive" parts become known by means of special investigations. The nonobservance of this viewpoint has, formerly, led to various devious speculations. In practice it is sufficient, as already stated, to establish regular deviations from additivity for certain definite constitutive peculiarities. These deviations in their turn are again, for *purely calculational purposes*, considered as additive, where, for reasons of expediency, one may proceed differently from case to case. Thus, for example, the oxygen atom usually assumes a different atomic constant depending on whether it is present in simple union in a hydroxyl group, or in double bond union in a carbonyl group; in special cases still finer distinctions must be made between the atomic constants for simply bound hydroxyl and ether oxygen atoms. In the case of carbon one seeks aid in another way; the usually very marked deviations from the additive scheme that appear in the case of unsaturated compounds are established and accounted for by an additional value or *increment* for the double and triple bonds, respectively. In this method of calculation then, bonding constants for certain types of bonds are used alongside of the atomic constants; the constant for the simple bond is thereby set formally equal to zero. The possibility of proceeding thus is always given when the additivity for a simple bonding of the atoms is fulfilled sufficiently well, for then one can simply distribute the value of the simple bond over the various atomic constants. This is true for the majority of the physical constants, in particular just for carbon, while oxygen and nitrogen frequently do not fit the additive scheme so well even in the case of simple bond compounds.

More will be said of this in detail in our discussion of the various physical properties, in particular of the molecular refractions (Cf. pp. 220 etc.). In general, one can, in the case of a substance of still unknown constitution, determine from the deviations shown by the properties of the substance from the additive scheme what are its characteristic constitutional peculiarities.



(b) *Heats of Combustion and Energy Content*

In the case of a property more or less nearly additive over a wide range of substances or conditions, it is useful to take the additive scheme as the starting point for theoretical considerations. Such a property is the already mentioned example of the heat of combustion of organic compounds. The values obtained in the determination of *heats of combustion* yield the almost exclusive material for a comparison of the *energy contents* of organic compounds\*. Such comparisons have been carried out already in earlier sections for several important problems: in the case of the cycloparaffins or polymethylenes, stereoisomeric compounds, conjugated and non-conjugated systems, aromatic and unsaturated compounds. The constitutional differences between individual compounds (or rather classes of compounds) were brought out there by the systematic deviations from an otherwise generally additive scheme. In general it is found that, as already emphasized previously (Vol. I, p. 94), the molar heat of combustion is additive; it increases then from member to member in a homologous series by approximately the same amount, varying little from one class of compound to the next, as for example among the homologous hydrocarbons, alcohols, mono- and dicarboxylic acids, and amounts to about 156—158 Cal per methylene,  $\text{CH}_2$ , group. Structural isomers with like types of bonds between the atoms, as well as stereoisomers, have usually, therefore, almost the same, or not very different, heats of combustion. As soon, however, as we deal with isomers with various types of bonds, considerable differences may arise. That is true not only for the comparison of isomers with simple as well as for those with multiple bonds, as for example for cyclohexane and hexene; here the compound with the double or the triple bond always exhibits a higher heat of combustion. But even in the case of substances with only simple bonds considerable differences may also occur, if they do not contain the same numbers of like bonds. Thus, for example, the heats of combustion of the isomers of  $\text{C}_2\text{H}_6\text{O}$ , ethyl alcohol and dimethyl ether, are different. These differences can be understood without further ado if, as already mentioned, we conceive of the combustion process as taking place in stages: first the dissolution or breaking of all bonds, and then the combustion of the thus-liberated free atoms. The latter always yields the same value for isomers. The first-mentioned energy term is however different for ethyl alcohol and dimethyl ether: in ethyl alcohol 8 bonds, 5  $\text{C—H}$ , 1  $\text{C—C}$ , 1  $\text{C—O}$ , and 1  $\text{O—H}$ -bond must be broken; in dimethyl ether likewise

\* A detailed treatment, from the historical side as well as the theoretical and experimental, may be found in E. BERNER, *A Contribution to the Thermochemistry of Organic Compounds* (Oslo, 1926).