DIPOLE MOMENTS IN ORGANIC CHEMISTRY

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PLENUM PRESS • NEW YORK–LONDON • 1970

Library of Congress Catalog Card Number 69-17901

SBN 306-30408-2

The original Russian text was first published by Khimiya Press in Leningrad in 1968. The present translation is published under an agreement with Mezhdunarodnaya Kniga, the Soviet book export agency.

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ДИПОЛЬНЫЕ МОМЕНТЫ

DIPOL'NYE MOMENTY

© 1970 Plenum Press, New York
A Division of Plenum Publishing Corporation
227 West 17th Street, New York, N.Y. 10011

United Kingdom edition published by Plenum Press, London
A Division of Plenum Publishing Corporation, Ltd.
Donington House, 30 Norfolk Street, London W.C. 2, England

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DIPOLE MOMENTS
IN ORGANIC CHEMISTRY

PHYSICAL METHODS IN ORGANIC CHEMISTRY

B. I. Ionin and B. A. Ershov
NMR Spectroscopy in Organic Chemistry, 1970

V. I. Minkin, O. A. Osipov, and Yu. A. Zhdanov
Dipole Moments in Organic Chemistry, 1970

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Preface

In accordance with the aims of the series "Physical Methods in Organic Chemistry," of which this book forms part, the authors' main aim was a systematic account of the most important methods of using the method of dipole moments in organic chemistry and interpreting its results in practice.

Since 1955, when two monographs devoted to the fundamentals and applications of the dipole moment method appeared simultaneously (C. P. Smyth, Dielectric Behavior and Structure, McGraw-Hill, New York; and J. W. Smith, Electric Dipole Moments, Butterworths, London), no generalizing studies of this type have appeared in the Russian and foreign literature. Nevertheless, it is just in this period that almost half of all publications on the structure and properties of organic compounds by means of the dipole moment method have appeared.

During this time, the principles of the method of measurement and the physical theory of the method have not undergone fundamental changes. Consequently, in giving an account of these matters we considered it sufficient to give a very short introduction to the theory of the method that is not burdened with details of the mathematical derivations and the strict formalism of the theory of dielectrics which are hardly used in the applications of the method that are of interest to the organic chemist (Chapter I).

In Chapter II the experimental methods of determining dipole moments are discussed in detail. Here the main attention has been devoted to the method of determining dipole moments in solutions in nonpolar solvents, which is the method most widely used for studying organic compounds. Here again, intermediate stages in the calculations are not given and all the formulas necessary for treating the results of measurement are given in a form directly suitable for carrying out the calculations.

In none of the published handbooks on dipole moments has the numerical apparatus of the method which is necessary for the structural interpretation of the results of the determinations been given systematically. In our opinion, it is partly for this reason that it is frequently possible to come across the idea of the excessively limited nature of the method in the study of fine features of the steric and electronic structure of organic compounds. The material collected in Chapter III should fill in this gap to a certain extent and facilitate the analysis of the dipole moments of organic compounds.

Chapters IV and V consider the fields of the traditional application of the method of dipole moments in organic chemistry: investigations of the spatial and electronic structure of molecules. In contrast to preceding monographs and reviews on dipole moments the material is arranged systematically not according to the type of organic compounds but according to the nature of the structural problems: conformational analysis, internal rotation, various types of electronic effects, and so on. Such an approach to a consideration of the applications of the method, it appears to us, corresponds more accurately to the spirit of modern physical organic chemistry.

The possibilities presented by the dipole moment method for studying some specific problems of the structure of organic compounds (tautomerism, the hydrogen bond, and other types of intermolecular interactions) are considered in Chapter VI. A special position is occupied by a section on the dipole moments of organic compounds in electronically excited states.

The scope and purpose of the monograph have not permitted adequate attention to be devoted to a whole series of questions having direct relationship with the method of dipole moments. This relates in the first place to the principles of the construction of the measuring apparatus. Readers with a special interest in this field we must refer to the books by Smyth and Smith already mentioned and also to the extremely detailed review in the third volume of the series "Technique of Organic Chemistry" (A. Weissberger, ed., Wiley, New York). However, we hope that we have succeeded in selecting those branches that are of the greatest interest for the organic chemist in his current work.

Chapters I and II were written by O. A. Osipov, Chapter III by V. I. Minkin, Chapters IV and V by V. I. Minkin and Yu. A. Zhdanov, and Chapter VI by V. I. Minkin and O. A. Osipov.

We shall be sincerely grateful to receive any information concerning deficiencies in the book.

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Dipole Moments and Some Special Problems of the Structure and Properties of Organic Compounds

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Chapter I

Basic Principles of the Theory of Dielectrics

1. Behavior of a Dielectric in a Static Electric Field*

An investigation of the electrical characteristics of a molecule gives important information on the distribution of charges in the molecule and provides the possibility of determining many properties of the molecule which depend on its electronic distribution. Those electrical properties of the molecule must be selected that are capable of a theoretical interpretation. The classical theory of the polarization of dielectrics shows that such properties of a molecule are exhibited in the behavior of the substance in an electric field.

Consider the behavior of a dielectric in a static electric field. Let us imagine a condenser with plane-parallel plates separated from one another by the distance r which is small in comparison with their linear dimensions. If the plates are charged and the surface density of the charges on them is $+\sigma$ and $-\sigma$, a practically uniform field is created in the condenser in a direction perpendicular to the surfaces of the plates. The strength of this field in vacuum will be

$$E_0 = 4\pi\sigma \tag{I.1}$$

---

* The theory of polarization is discussed in more detail in References [1-12].

Under these conditions, the difference in potential V arising between the plates of the condenser can be defined as

$$V = |E_0|r \tag{I.2}$$

Let us fill the space between the plates of the condenser with a dielectric, keeping the charge density on the plates of the condenser at its previous value. This leads to a fall in the potential difference between the plates of the condenser by the amount V/ε_s, where ε_s is the static dielectric constant of the substance. Since relation (I.2) remains valid, the strength of the electric field decreases by the same magnitude

$$E = \frac{4\pi\sigma}{\varepsilon_s} \tag{I.3}$$

Thus, the static dielectric constant may be considered as the ratio of the field strength in vacuum to the field strength of the condenser containing the dielectric:

$$\varepsilon_s = \frac{E_0}{E} \tag{I.4}$$

The static dielectric constant is easily expressed in terms of the capacitances of the condenser in vacuum and when it is filled with dielectric, since the capacitance is q/V. Here q is the charge density, σ, times the area of the condenser plates. Then we obtain

$$\varepsilon_s = \frac{C}{C_0} \tag{I.5}$$

where C_0 and C are, respectively, the capacitance of the condenser in vacuum and its capacitance when filled with the dielectric.

The dielectric constant is generally determined by measuring the capacitances C_0 and C [3, 5, 7, 8, 12, 13] and then using formula (I.5), except for those cases where measurements are carried out at very low or very high frequencies, for which other methods are used [5, 13].

From a macroscopic standpoint, the influence of an electric field on a dielectric, leading to an increase in the capacitance of the condenser, is equivalent to the charging of the two surfaces of the dielectric directly adjacent to the plates of the condenser with charges of opposite signs (Fig. 1).

Such an accumulation of uncompensated negative charges on the surface of the dielectric adjacent to the positively charged plate and of positive charges adjacent to the negatively charged plate of the condenser leads to a partial decrease in the original

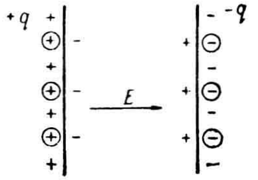

Fig. 1. Macroscopic description of the change in the potential difference on introduction of a dielectric between the plates of a plane-parallel condenser.

charges q. This follows from equations (I.1) and (I.3), a combination of which leads to the expression

$$P = \sigma \frac{\varepsilon_s - 1}{\varepsilon_s} \qquad (I.6)$$

The magnitude P must be considered as the surface charge density on the dielectric.

The cause of the increase in the capacitance of the condenser is the polarization of the dielectric under the action of the applied electric field.

In the absence of an electric field, the substance as a whole is electrically neutral and in any small volume of it (which must, however, contain a sufficiently large number of molecules) the centers of all the positive and negative charges coincide. Under the action of the applied field, a displacement of the centers of gravity of the charges by some distance $\vec{l}$ takes place and an electric dipole appears.* Such a displacement of the charges under the action of a field is called the electric polarization $\vec{p}$ of the substance. The phenomenon of polarization can be considered by ascribing to each small volume of the dielectric some induced dipole moment. This is valid since the electric dipole moment can characterize not only the electric state of the individual molecule† but also that of some macroscopic volume of the dielectric consisting of a large number of molecules. Then, for unit volume of the dielectric (1 cm^3) the magnitude of the induced dipole moment can be given as

$$\vec{p} = \sum_i e_i \vec{l}_i \qquad (I.7)$$

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* In the general case, by an electric dipole must be understood any system consisting of electric charges q equal in magnitude and opposite in sign separated by a distance vector $\vec{l}$. The magnitude of such a dipole is defined by its electric moment:

$$\vec{\mu} = q\vec{l}$$

† The behavior of an individual molecule in an electric field will be considered below.

where $\vec{p}$ is the polarization per unit volume. Here the summation is extended over all the charges (electrons and nuclei) present in unit volume of the dielectric.

It follows from what has been said above that the field within the dielectric $\vec{E}$ must be composed of the field $\vec{E}_0$, created by the charges q on the plates of the condenser when the dielectric substance is absent and the field induced by the dipoles, which is in the opposite direction to $\vec{E}_0$.

According to the laws of electrostatics, the field created by the induced dipoles is $-4\pi\vec{p}$. Consequently, for the field within the dielectric

$$\vec{E}=\vec{E}_0-4\pi\vec{p} \tag{I.8}$$

where $\vec{E}$ is due both to the charge density on the plates of the condenser and to the charge density on the surface of the dielectric.

In the macroscopic theory of dielectrics, the vector $\vec{D}$, which is called the electric displacement or the electric induction, is introduced:

$$\vec{D}=\vec{E}+4\pi\vec{p} \tag{I.9}$$

The connection between the electric induction and the field strength within a dielectric can also be determined on the basis of equation (I.4):

$$\vec{D}=\vec{E}\varepsilon_s \tag{I.10}$$

As can be seen from (I.10) the magnitude $\vec{D}$ is proportional to $\vec{E}$, the proportionality factor being the static dielectric constant. The difference between $\vec{D}$ and $\vec{E}$ depends on the degree of polarizability of the dielectric in an electric field. In vacuum, where there is no polarization, $\vec{D}=\vec{E}$ and $\varepsilon_s = 1$.

Thus, in the macroscopic theory, the electric field in dielectrics is described by means of two quantities: the macroscopic field $\vec{E}$ and the electric induction $\vec{D}$.

From equations (I.9) and (I.10), we obtain

$$\vec{p} = \frac{\varepsilon_s - 1}{4\pi} \vec{E} \tag{I.11}$$

Formula (I.11) establishes a connection between the dielectric constant, the field $\vec{E}$, and the polarization of the dielectric $\vec{p}$. The polarization vector is proportional to the field and has the same direction. However, this is valid only for isotropic media. In anisotropic media the direction of the polarization vector may or may not coincide with the direction of the field. In this case, the absolute magnitude of the vector $\vec{p}$ depends not only on the absolute value of the vector $\vec{E}$, but also on its direction with respect to the principal axes of the dielectric.

The further consideration of the polarization of a dielectric $\vec{p}$ requires the use of molecular ideas. In order to connect the macroscopic behavior of a dielectric with the properties of its individual molecules and to establish the polarization mechanism it is necessary to determine how an isolated neutral molecule of the dielectric will behave in an electric field. From this point of view, all dielectrics may be divided into nonpolar and polar media. In the former, the molecules possess electrical symmetry and the centers of gravity of the positive and of the negative charges coincide. Polar dielectrics, on the other hand, are constructed of electrically asymmetrical molecules in which the centers of gravity of the positive and of the negative charges are located at some distance l from one another and form an electric dipole. Thus, nonpolar molecules do not possess a dipole moment in the absence of a field, while polar molecules have a permanent dipole moment independent of the field.

Let us first consider the behavior of molecules possessing no permanent dipole moments.

Under the action of an applied electric field, a process of polarization takes place not only in any small volume of the dielectric but also in each individual molecule, whether or not it has a permanent dipole moment in the absence of a field. The action of the field leads to the appearance in the molecule of some induced dipole moment $\vec{m}$, the magnitude of which is proportional to the strength of the mean macroscopic field $\vec{E}$

$$\vec{m} = \alpha\vec{E} \tag{I.12}$$

where α is a proportionality factor, the so-called polarizability of the molecule. It is a measure of the mobility of the charges in the molecule and characterizes their relative displacement under the action of the field.

If unit volume (1 cm^3) contains n molecules possessing the induced dipole moment $\vec{m}$, the polarization $\vec{p}$ will be

$$\vec{p} = n\vec{m} \tag{I.13}$$

Using equations (I.11), (I.12), and (I.13), it is possible to establish the connection between the static dielectric constant, the polarizability of the molecule, and the strength of the mean macroscopic field:

$$\vec{p} = n\vec{m} = n\alpha\vec{E} = \frac{\varepsilon_s - 1}{4\pi}\vec{E} \tag{I.14}$$

whence

$$\varepsilon_s = 1 + 4\pi n\alpha$$

It follows from the last expression that the magnitude of the static dielectric constant is the greater the greater the density of the substance and the greater the polarizability of the molecule.

Equation (I.14) is not strictly correct and has a limited application. To a first approximation, it can be applied to gases at sufficiently low pressures when the distance between the molecules is so large that it is possible to neglect the action of the electrostatic field of the surrounding molecules on the particular molecule with which we are dealing. This condition means that the polarization due to the introduction of a gaseous dielectric is extremely slight, so that the dielectric constant differs very little from unity.

When the distance between neighboring molecules is comparable with the dimensions of the molecules themselves (gases at high densities, liquids) it is no longer possible to neglect the action of the electrostatic field of the surrounding molecules on the particular molecule with which we are dealing. In this case, the dielectric medium can no longer be regarded as a continuous medium with the dielectric constant ε_s as was assumed in the macroscopic discussion. Under the action of the external field, the electrostatic field created by the surrounding molecules is distorted, since the

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