ATOMIC CHARGES, BOND PROPERTIES, AND MOLECULAR ENERGIES

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Published by John Wiley & Sons, Inc., Hoboken, New Jersey
Published simultaneously in Canada

Library of Congress Cataloging-in-Publication Data:

Fliszár, Sándor.
Atomic charges, bond properties, and molecular energies / Sándor Fliszár.
p. cm.
Includes index.
ISBN 978-0-470-37622-5 (cloth)
1. Chemical bonds. I. Title.
QD461.F536 2009
541′.224--dc22

2008021431

Printed in the United States of America
10 9 8 7 6 5 4 3 2 1

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PREFACE

This book is about atomic charges, chemical bonds, and bond energy additivity. However, nuclear magnetic resonance, inductive effects, zero-point and heat content energies, and other topics are an integral part of this study, to achieve our goals.

The electronic charges, the bond energies, and—way down the line—the energy of atomization and the enthalpy of formation of organic molecules are what we shall calculate with chemical accuracy, in a simple manner.

Of course, new ideas have to be implemented, in terms of both bond energies and the calculation of atomic charges; the formula describing the energy of a chemical bond in a ground-state molecule—the "intrinsic" bond energy—translates intuitive expectations, namely, that the energy of a bond formed by atoms k and l should depend on the amount of electronic charge carried by these atoms. The all-important relationship between the *intrinsic bond energies*—which apply for bonds in molecules at equilibrium—and the corresponding familiar *bond dissociation energies*—which refer specifically to the process of bond breaking—is also described.

Intrinsic bond energies and bond dissociation energies meet different practical needs. The former play an important role in the description of ground-state molecules. Dissociation energies, on the other hand, come into play when molecules undergo reactions. Now, any interaction between a molecule and its environment (such as complex formation or the adsorption onto a metallic surface, or hydrogen bonding, for example) affects its electron distribution and thus the energies of its chemical bonds. If we figure out the relationship between dissociation and intrinsic bond energies, we could begin to understand how the environment of a molecule can promote or retard the dissociation of one or another bond of particular interest in that molecule. This outlook hints at a rich potential of future research exploiting charge analyses to

gain insight into *local* molecular properties, specifically, into bond energies, first, and, going from there, into matters of great import regarding the dissociation of chemical bonds.

Our methods, like many others, do not answer all possible questions; plain quantum chemistry is undeniably the procedure of choice. But what our methods do, they surely do it with great accuracy and with a chemical insight that is not offered by traditional approaches and, moreover, in an extremely inexpensive manner, in regard to computational resources and costs. Applications are presented for saturated acyclic and cyclic hydrocarbons, amines, alcohols, ethers, aldehydes and ketones, and ethylenic and aromatic hydrocarbons. The results surely are impressive. Beyond offering new perspectives to old problems, the wealth of details given here hopefully lays fertile grounds for future breakthroughs along the simple lines advocated in this work. And while keeping the text as accessible as possible, the bibliography is richly designed, to assist interested readers in going more and more deeply into the wheelwork of the matter. With that goal in mind, a compendium of user-friendly final formulas is offered in the Appendix.

A few words about this book are in order. It is about chemistry (or, should I say physical organic chemistry?) that exploits quantum-mechanical methods. First-year graduate and advanced undergraduate introductory courses in quantum chemistry offer the required background. A most concise presentation—not an explanation—of the required quantum-mechanical techniques is offered, but a large part of this book is accessible without mastering them. The physics are given with sufficient details, which, I hope, are easy to follow. The whole thing—hopefully with the future aid of interested readers—adds powerful new investigative tools in areas of great import that help the reader understand chemical principles and predict properties.

This is the present for the future.

SÁNDOR FLISZÁR

DEDICATION AND ACKNOWLEDGMENTS

I wish to dedicate this work to my students and postdoctoral fellows who made things possible: Marie-Thérèse Béraldin, Jacques Bridet, Jean-Louis Cantara, Guy Cardinal, Michel Comeau, Geneviève Dancausse, Normand Desmarais, Anikó Foti, Marielle Foucrault, Annik Goursot, Jacques Grignon, Hervé Henry, Gérard Kean, Claude Mijoule, Camilla Minichino, Andrea Peluso, François Poliquin, Réal Roberge, and Édouard C. Vauthier. I also express my heartfelt thanks for active help, advice, patience, and friendship to Professors Giuseppe Del Re, Vincenzo Barone, Jean-Marie Leclercq, Simone Odiot, and Dennis Salahub. But my special thanks go to Steve Chrétien for his great dedication in helping me with most of the numerical calculations rooted in Del Re's theory that support the present work. It was my fortune to have him as a coworker and, I think, as a friend. And had it not been for the patient and skilled help of Édouard Vauthier, and his friendship, many of these pages could not have been written. I am also indebted to my daughter Saskia for helpful suggestions and corrections to this text. I also wish to thank Mr. Xiao-Gang Wang for his kindness and skillful help. Last but not least, I include Signora Dora and Don Gaetano Lampo in this dedication. These fine people made me a better person by teaching me important things, such as the *true* tolerance that is so uniquely part of Neapolitan culture. They also made me a little, but just a little, fatter.

Now that everything is behind us, I begin to understand how we benefited from exceptional circumstances when most important scientific facts were harvested with an incredible timing; the ink had barely dried when they came to fill essential

needs in the fabric of our work. We could not have done it otherwise. I feel deeply in debt and wish to express my sincere appreciation to my fellow chemists and physicists recalling the wording of an old chinese proverb: *When you drink the water, don't forget the source*. Thank you. I won't forget.

SÁNDOR FLISZÁR

PART I

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