Halogen atoms in organic compounds can typically be found at the periphery of molecules. For this reason, they are ideally positioned to be involved in intermolecular interactions. Indeed, halogen atoms are frequently involved in a wide variety of non-covalent interactions which can be remarkably different regarding their energetic and geometric features. Theoretical studies predict that the electron density distribution around halogen atoms forms an ellipsoid elongated in the direction perpendicular to the covalent bond axis. A clear trend of increasing electropositive potential develops along the covalent bond axis upon increasing the polarizability and atomic mass of the halogen. Experimental results confirm this anisotropic distribution and prove the amphoteric character of halogens. This can produce interactions in a direction perpendicular to the covalent bond axis when the halogen is the electron donor (Lewis base), and along the axis when the halogen is the electron acceptor (Lewis acid).

This book focuses on the interactions wherein halogens work as electrophilic species and interact with electron rich sites (namely, electronegative partners). Of the numerous non-covalent interactions involving halogens, this particular subset is typically referred to as halogen bonding. The book begins by introducing theoretical calculations on the characteristics of halogen bonding (A. Karpfen), then focuses on the adducts wherein the electron donor is a lone pair possessing species (n donor). The complexes formed by halogens and interhalogens in the gas (A. Legon) and solid phase (W. T. Pennington et al.) are presented and the role of halocarbons in halogen bonding-based crystal engineering is discussed (P. Metrangolo, G. Resnati et al.). A chapter exploring the complexes in which halogen atoms interact with π electron donors (J. K. Kochi et al.) concludes the part of the book that deals with the generalities of halogen bonding. In contrast, the last two chapters of this book discuss halogen bonded adducts endowed with useful applicative properties. Among the many novel applications of halogen bonding, liquid crystals (D. Bruce) and conducting or magnetic materials (M. Fourmigue) are discussed as prototypical examples.

The findings presented throughout this book consistently converge towards the use of the term halogen bonding, independent of the energy of the interaction or its prevailing character, whether electrostatic or charge-transfer. The effectiveness of a scientific concept and the associated terminology often rest
on an optimized balance between generality, resulting in a wide applicability, and specificity, enabling it to predict specific phenomena. In this respect, it is our opinion that the concept of halogen bonding is beneficial if it is defined as comprehensively as possible, while assigning the specific role of the positive site in the interaction to the halogen. At one extreme, the term can be used for interactions in which a very strong polarity difference exists between interacting partners (as it is the case of dihalogen/halide anion complexes, e.g., I$_{3}^{-}$). At the other extreme, the term halogen bonding can be used for interactions wherein the polarity difference between the interacting partners is very small (e.g., in the triangular bromocarbon trimer synthon).

This book is a first in the field of halogen bonding. Focussing on interactions in which halogens work as the electrophilic sites, this book identifies the boundaries of the concept of halogen bonding. In addition, it organizes the diversified profile of intermolecular interactions involving halogens.

In order to reflect the differences in geometric and electronic parameters, a term different from halogen bonding might be used to address interactions wherein halogens work as electron donor sites. Halide bonding could be considered for this purpose, however, the best terminology to be used will emerge from the increasing interest in interactions involving halogens and will be spontaneously identified by the consensus of the scientific community.

The field of halogen bonding is still in its infancy. Nevertheless, this book proves its potential in the numerous and diverse fields in which recognition and self-assembly processes are crucial. Hopefully, this book will prompt new studies in the field that deepen the basic understanding of halogen interactions and implement its potential in the design of useful materials.

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Pierangelo Metrangolo

Giuseppe Resnati
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