

Viktor V. Zhdankin

# Hypervalent Iodine Chemistry

Preparation, Structure and  
Synthetic Applications of  
Polyvalent Iodine Compounds

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## Preparation, Structure and Synthetic Applications of Polyvalent Iodine Compounds

**Viktor V. Zhdankin**

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**WILEY**

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# **Hypervalent Iodine Chemistry**



# Preface

Iodine is the heaviest non-radioactive element in the Periodic Table that is classified as a nonmetal and it is the largest, the least electronegative and the most polarizable of the halogens. It formally belongs to the main group p-block elements; however, the bonding description, structural features and reactivity of iodine compounds differ from the light main-group elements. The electronic structure of polyvalent iodine is best explained by the hypervalent model of bonding and, therefore, in modern literature organic compounds of trivalent and pentavalent iodine are commonly named as hypervalent iodine compounds. The reactivity pattern of hypervalent iodine in many aspects is similar that of transition metals – the reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination and ligand coupling, which are typical of transition metal chemistry.

Since the beginning of the twenty-first century, the organic chemistry of hypervalent iodine compounds has experienced an unprecedented, explosive development. Hypervalent iodine reagents are now commonly used in organic synthesis as efficient multipurpose reagents whose chemical properties are similar to derivatives of mercury, thallium, lead, osmium, chromium and other metals, but without the toxicity and environmental problems of these heavy metal congeners. One of the most impressive recent achievements in the field of iodine chemistry has been the discovery of hypervalent iodine catalysis.

This book is the first comprehensive monograph covering all main aspects of the chemistry of organic and inorganic polyvalent iodine compounds, including applications in chemical research, medicine and industry. The introductory chapter (Chapter 1) provides a historical background and describes the general classification of iodine compounds, nomenclature, hypervalent bonding, general structural features and general principles of reactivity of polyvalent iodine compounds. Chapter 2 gives a detailed description of the preparative methods and structural features of all known classes of organic and inorganic derivatives of polyvalent iodine. Chapter 3, the central chapter of the book, deals with the applications of hypervalent iodine reagents in organic synthesis. Chapter 4 describes the most recent achievements in hypervalent iodine catalysis. Chapter 5 deals with recyclable polymer-supported and nonpolymeric hypervalent iodine reagents. Chapter 6 covers the “green” reactions of hypervalent iodine reagents, including solvent-free reactions, reactions in water and reactions in ionic liquids. The final chapter (Chapter 7) provides an overview of important practical applications of polyvalent iodine compounds in medicine and in industry.

This book is aimed at all chemists interested in iodine compounds, including academic and industrial researchers in inorganic, organic, physical, medicinal and biological chemistry. It will be particularly useful to synthetic organic and inorganic chemists, including graduate and advanced undergraduate students. The book also covers the green chemistry aspects of hypervalent iodine chemistry, including the use of water as solvent, reactions under solvent-free conditions, recyclable reagents and solvents and catalytic reactions, which makes it especially useful for industrial chemists. The last chapter provides a detailed summary of practical applications of polyvalent iodine compounds, including various industrial applications, biological activity and applications of iodonium salts in PET (positron emission tomography) diagnostics; this chapter should be especially useful for medical and pharmaceutical researchers. Overall, the book is aimed at a broad, multidisciplinary readership and specialists working in different areas of chemistry, pharmaceutical and medical sciences and industry.

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# 1

## Introduction and General Overview of Polyvalent Iodine Compounds

### 1.1 Introduction

Iodine is a very special element. It is the heaviest non-radioactive element in the Periodic Table classified as a non-metal and it is the largest, the least electronegative and the most polarizable of the halogens. It formally belongs to the main group, p-block elements; however, because of the large atom size, the bonding description in iodine compounds differs from the light main group elements. In particular, the interatomic  $\pi$ -bonding, typical of the compounds of light p-block elements with double and triple bonds, is not observed in the compounds of polyvalent iodine. Instead, a different type of bonding occurs due to the overlap of the 5p orbital on the iodine atom with the appropriate orbitals on the two ligands (L) forming a linear L–I–L bond. Such a three-center-four-electron (3c-4e) bond is commonly referred to as a “hypervalent bond” [1]. The hypervalent bond is highly polarized and is longer and weaker than a regular covalent bond and the presence of hypervalent bonding leads to special structural features and reactivity pattern characteristic of polyvalent iodine compounds. In current literature, synthetically useful derivatives of polyvalent iodine are commonly named as hypervalent iodine reagents. The reactivity pattern of hypervalent iodine in many aspects is similar to the reactivity of transition metals and the reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, ligand exchange, reductive elimination and ligand coupling, which are typical of transition metal chemistry.

Iodine was first isolated from the ash of seaweed by the industrial chemist B. Courtois in 1811 and was named by J. L. Gay Lussac in 1813 [2, 3]. Its name derives from the Greek word  $\iotaώδες$  (iodes) for violet, reflecting the characteristic lustrous, deep purple color of resublimed crystalline iodine. Various inorganic derivatives of polyvalent iodine in oxidation states of +3, +5 and +7 were prepared as early as the beginning of the nineteenth century. For example, iodine trichloride was first discovered by Gay Lussac as the result of treating warm iodine or iodine monochloride with an excess of chlorine [4]. In the same paper [4], the preparation of potassium iodate by the action of iodine on hot potash lye was described. The inorganic chemistry of polyvalent iodine has been summarized in numerous well-known texts [3, 5–8]. A detailed review on the history of iodine and all aspects of its chemistry and applications commemorating two centuries of iodine research was published in 2011 by Kuepper and coauthors [9].

Most of the world's production of iodine comes from the saltpeter deposits in Chile and natural brines in Japan. In Chile, calcium iodate is found in caliche deposits extracted from open pit mines in the Atacama Desert. Applying an alkaline solution to the caliche yields sodium iodate and iodine is obtained from the sodium iodate by reduction with sulfur dioxide. In Japan, iodine is a by-product of the production of natural gas, which is extracted from brine deposits a mile or two below ground. Iodine is recovered from the brines by one of the following two methods. In the blowout process elemental iodine is liberated as a result of the reaction of chlorine with sodium iodide in the brines. Elemental iodine is blown out of the brine with air and then purified in subsequent reaction steps. The second method, ion exchange, involves recovery of dissolved iodine from oxidized brines using anion-exchange resins packed in columns. In 2010, Chile produced 18 000 metric tons of iodine, compared to Japan's output of 9800 metric tons. Chile has reserves of 9 million metric tons, some 60% of the world's total reserves of iodine [10].

Iodine plays an important role in many biological organisms and is an essential trace element for humans. In the human body, iodine is mainly present in the thyroid gland in the form of thyroxine, a metabolism-regulating hormone. In natural organic compounds, iodine occurs exclusively in the monovalent state. The first polyvalent organic iodine compound, (dichloroiodo)benzene, was prepared by the German chemist C. Willgerodt in 1886 [11]. This was rapidly followed by the preparation of many others, including (diacetoxyiodo)benzene [12] and iodosylbenzene [13] in 1892, 2-iodoxybenzoic acid (IBX) in 1893 [14] and the first examples of diaryliodonium salts reported by C. Hartmann and V. Meyer in 1894 [15]. In 1914 Willgerodt published a comprehensive book describing nearly 500 polyvalent organoiodine compounds known at that time [16].

Research activity in the area of polyvalent organoiodine compounds during the period between 1914 and 1970s was relatively low and represented mainly by valuable contributions from the laboratories of I. Masson, R. B. Sandin, F. M. Beringer, K. H. Pausacker, A. N. Nesmeyanov and O. Neilands. Only three significant reviews were published during this period, most notably the reviews by Sandin [17] and Banks [18] published in *Chemical Reviews* in 1943 and 1966, respectively and a comprehensive tabulation of the physical properties of polyvalent iodine compounds published in 1956 by Beringer [19].

Since the early 1980s interest in polyvalent organoiodine compounds has experienced a renaissance. This resurgence of interest in multivalent organic iodine has been caused by the discovery of several new classes of polyvalent organoiodine compounds and, most notably, by the development of useful synthetic applications of some of these compounds, which are now regarded as valuable organic reagents known under the general name of hypervalent iodine reagents. The foundation of modern hypervalent iodine chemistry was laid in the 1980s by the groundbreaking works of G. F. Koser, J. C. Martin, R. M. Moriarty, P. J. Stang, A. Varvoglis and N. S. Zefirov.

Important contributions to the development of hypervalent iodine chemistry in the 1990s were made by the research groups of A. Varvoglis, N. S. Zefirov, L. M. Yagupolskii, A. R. Katritzky, R. A. Moss, J. C. Martin, D. H. R. Barton, R. M. Moriarty, G. F. Koser, P. J. Stang, H.-J. Frohn, T. Umemoto, M. Yokoyama, Y. Kita, M. Ochiai, T. Okuyama, T. Kitamura, H. Togo, E. Dominguez, I. Tellitu, J. D. Protasiewicz, A. Kirschning, K. S. Feldman, T. Wirth, S. Quideau, S. Hara, N. Yoneda, L. Skulski, S. Spyroudis, V. V. Grushin, V. W. Pike, D. A. Widdowson and others. During the 1980s–1990s, hypervalent iodine research was summarized in several reviews and books. Most notable were the two books published in 1992 and 1997 by A. Varvoglis: the comprehensive monograph *The Organic Chemistry of Polycoordinated Iodine* [20] and a book on the application of hypervalent iodine compounds in organic synthesis [21]. Several general reviews [22–28], numerous book chapters [29–34] and specialized reviews on phenyliodonium(III) carboxylates [35, 36], [hydroxy(tosyloxy)iodo]benzene [37], the chemistry of iodonium salts [38], electrophilic perfluoroalkylations [39], application of hypervalent iodine in the carbohydrate chemistry [40], hypervalent iodine oxidations [41–43], fluorinations using hypervalent iodine fluorides [44], hypervalent iodine compounds as free radical precursors [45], synthesis of heterocyclic compounds using organohypervalent iodine reagents [46] and the chemistry of benziodoxoles [47] were also published during 1980s and 1990s.



Since the beginning of the twenty-first century, the chemistry of organohypervalent iodine compounds has experienced explosive development. This surge in interest in iodine compounds is mainly due to the very useful oxidizing properties of hypervalent iodine reagents, combined with their benign environmental character and commercial availability. Iodine(III) and iodine(V) derivatives are now routinely used in organic synthesis as reagents for various selective oxidative transformations of complex organic molecules. Numerous reviews and book chapters summarizing various aspects of hypervalent iodine chemistry have been published since 2000 [48–122]. A book edited by T. Wirth on the application of hypervalent iodine in organic synthesis was published in 2003 [123]. Starting in 2001, the International Conference on Hypervalent Iodine Chemistry has regularly been convened in Europe, the Society of Iodine Science (SIS) holds annual meetings in Japan and the American Chemical Society presents the National Award for Creative Research and Applications of Iodine Chemistry sponsored by SQM S.A. biennially in odd-numbered years. The most impressive modern achievements in the field of organoiodine chemistry include the development of numerous new hypervalent iodine reagents and the discovery of catalytic applications of organoiodine compounds. The discovery of similarities between transition metal chemistry and hypervalent iodine chemistry and, in particular, the development of highly efficient and enantioselective catalytic systems based on the iodine redox chemistry have added a new dimension to the field of hypervalent iodine chemistry and initiated a major increase in research activity, which is expected to continue in the future.

## 1.2 Classification and Nomenclature of Polyvalent Iodine Compounds

Iodine can form chemical compounds in oxidation states of +3, +5 and +7. The six most common structural types of polyvalent iodine species are represented by structures 1–7 (Figure 1.1). Species 2–7 can be generally classified using the Martin–Arduengo *N-X-L* designation for hypervalent molecules [124, 125], where *N* is the number of valence electrons formally assignable to the valence shell of the central atom, *X*, either as unshared pairs of electrons or as pairs of electrons in the sigma bonds joining a number, *L*, of ligands to the atom *X*. Structure 1, the iodonium ion, formally does not belong to hypervalent species since it has only eight valence electrons on the iodine atom; however, in the modern literature iodonium salts are commonly treated as ten-electron hypervalent compounds by taking into account the closely associated anionic part of the molecule. The first three species, structures 1–3, are conventionally considered as derivatives of trivalent iodine, while 4 and 5 represent the most typical structural types of pentavalent iodine. Structural types 6 and 7 are typical of heptavalent iodine; only inorganic compounds of iodine(VII), such as iodine(VII) fluoride (IF<sub>7</sub>), iodine(VII) oxyfluorides and the derivatives of periodic acid (HIO<sub>4</sub>) are known.

In the older literature, derivatives of iodine(III) were known under the general name of iodinanes, while compounds of pentavalent iodine were called periodinanes. According to the 1983 IUPAC recommendations “Treatment of variable valence in organic nomenclature (lambda convention)” [126], these old names were replaced by λ<sup>3</sup>-iodanes for iodine(III) and λ<sup>5</sup>-iodanes for iodine(V) compounds. In the lambda nomenclature,

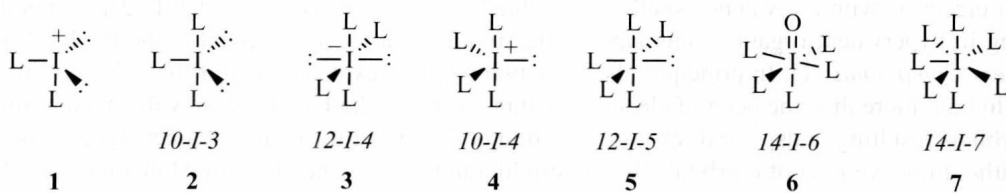


Figure 1.1 Typical structural types of polyvalent iodine compounds.

the symbol  $\lambda^n$  is used to indicate any heteroatom in nonstandard valence states ( $n$ ) in a formally neutral compound; for iodine the standard valence state is 1. The names  $\lambda^3$ -iodanes and  $\lambda^5$ -iodanes have found broad application in modern literature to indicate the general type of hypervalent iodine compounds and to specify the number of primary bonds at the iodine atom. The  $\lambda^3$ -iodane designation is particularly useful for naming iodonium salts, for example,  $\text{Ph}_2\text{ICl}$ , because it better reflects the actual structure of these compounds with a tricoordinated iodine atom [127].

Notably, however, the lambda nomenclature is not used for naming common hypervalent iodine reagents such as  $\text{PhICl}_2$ ,  $\text{PhI}(\text{OAc})_2$ ,  $\text{ArIO}$ ,  $\text{ArIO}_2$  and others. According to the 1979 IUPAC rules [128], “compounds containing the group  $-\text{I}(\text{OH})_2$  or derivatives of this group are named by adding the prefixes “dihydroxyiodo-”, “dichloroiodo-”, “diacetoxyiodo-”, etc. to the name of the parent compound” (IUPAC Rule C-106.3). Likewise, “compounds containing the group  $-\text{IO}$  or  $-\text{IO}_2$ , are named by adding the prefix “iodosyl-” or “iodyl-” (IUPAC Rule C-106.1) [128], which replaces prefixes “iodoso-” and “iodoxy-” used in the older literature. According to IUPAC Rule C-107.1 “cations of the type  $\text{R}^1\text{R}^2\text{I}^+$  are given names derived from the iodonium ion  $\text{H}_2\text{I}^+$  by substitution” [128]. In addition to the IUPAC recommended names, numerous common names and abbreviations are used for polyvalent iodine compounds; for example, about 15 different names have been used in the literature for  $\text{PhI}(\text{OAc})_2$  [20]. Table 1.1 summarizes commonly used names and abbreviations for several important organic and inorganic polyvalent iodine compounds.

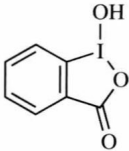
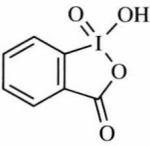
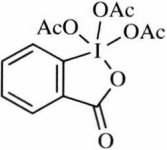
Organoiodine(III) compounds are commonly classified by the type of ligands attached to the iodine atom. The following general classes of iodine(III) compounds have found broad application as reagents in organic synthesis: (difluoroiodo)arenes **8**, (dichloroiodo)arenes **9**, iodosylarenes **10**, [bis(acyloxy)iodo]arenes **11**, aryl iodine(III) organosulfonates **12**, five-membered iodine heterocycles (benziodoxoles **13** and benziodazoles **14**), iodonium salts **15**, iodonium ylides **16** and iodonium imides **17** (Figure 1.2). The most important and commercially available representatives of aryl iodine(III) carboxylates are (diacetoxyiodo)benzene  $\text{PhI}(\text{OAc})_2$ , which has several commonly used abbreviations, such as DIB, PID, PIDA (phenyliodine diacetate), IBD, or IBDA (iodosobenzene diacetate) and [bis(trifluoroacetoxy)iodo]benzene  $\text{PhI}(\text{OCOCF}_3)_2$ , which is abbreviated as BTI or PIFA [(phenyliodine bis(trifluoroacetate))] (Table 1.1). The most important representative of aryl iodine(III) organosulfonates, the commercially available [hydroxy(tosyloxy)iodo]benzene  $\text{PhI}(\text{OH})\text{OTs}$ , is abbreviated as HTIB and is also known as Koser’s reagent.

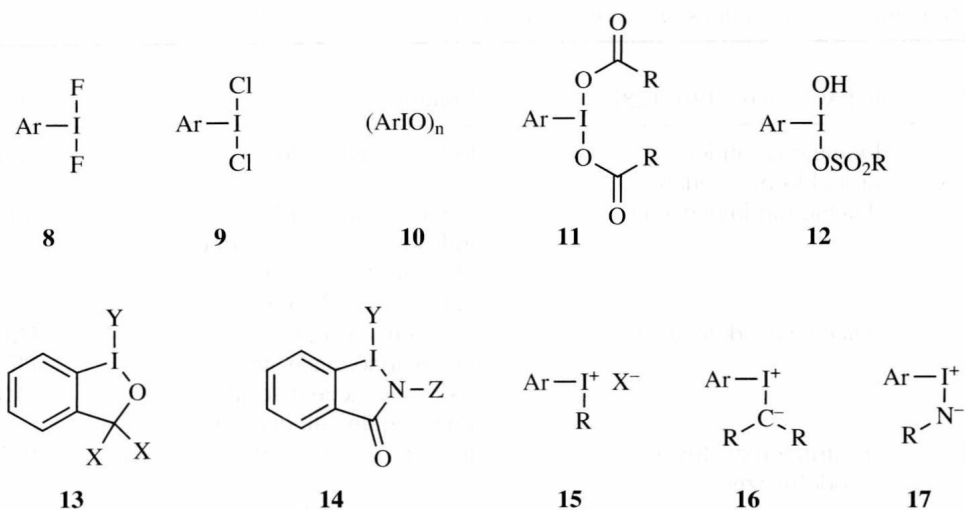
Organoiodine(V) compounds are represented by several common classes shown in Figure 1.3; all these compounds have found application as efficient oxidizing reagents. Particularly important in organic synthesis are noncyclic iodylarenes **18**, numerous five-membered heterocyclic benziodoxole derivatives **19** and **20**, including IBX and DMP (Table 1.1), pseudocyclic iodylarenes **21–23** and cyclic or pseudocyclic derivatives of 2-iodylbenzenesulfonic acid, **24–26**.

### 1.3 Hypervalent Bonding

The definition of “hypervalent” species as ions or molecules of the elements of Groups 15–18 bearing more than eight electrons within a valence shell was established by J. I. Musher in 1969 [129]. General aspects of bonding in hypervalent organic compounds were summarized by K.-y. Akiba in the book *Chemistry of Hypervalent Compounds* [1]. In principle, there are two possible explanations for the ability of main-group elements to hold more than the octet of electrons within a valence shell: (i) by the involvement of the higher-lying d orbitals resulting in  $\text{dsp}^3$  or  $\text{d}^2\text{sp}^3$  hybridization or (ii) by the formation of a new type of highly ionic orbital without involvement of d orbitals. In modern literature, it is generally agreed that the contribution of d orbitals is not essential to form hypervalent compounds and that hypervalent bonding is best explained by a molecular orbital description involving a three-center-four-electron bond.

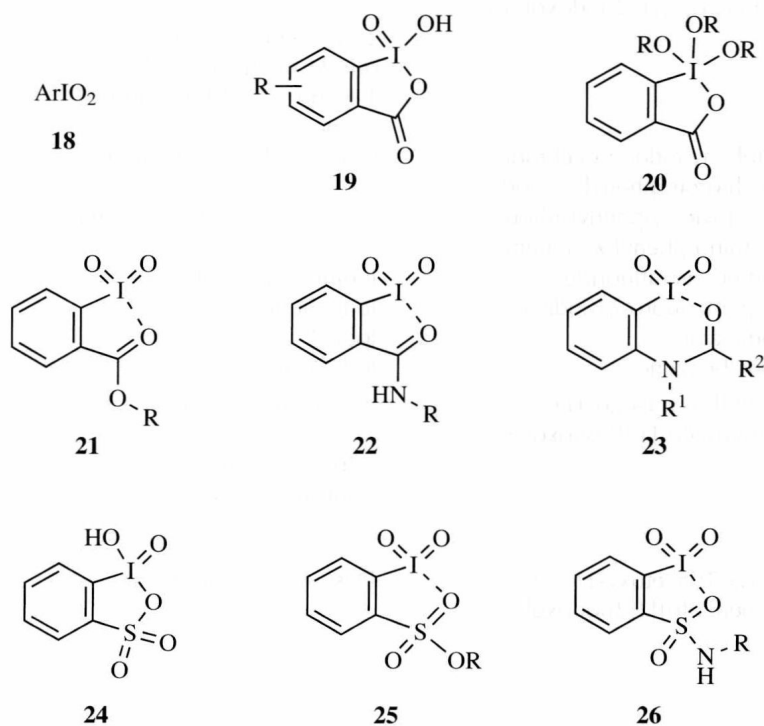
**Table 1.1** Names and abbreviations of important derivatives of polyvalent iodine.

Compound	IUPAC names [126, 128]	Common names	Common abbreviations
ICl <sub>3</sub>	Iodine trichloride or trichloro- $\lambda^3$ -iodane	Iodine(III) chloride	None
PhICl <sub>2</sub>	(Dichloroiodo)benzene	Iodobenzene dichloride Iodosobenzene dichloride Phenyliodo dichloride Phenyliodine(III) dichloride	IBD
PhI(OAc) <sub>2</sub>	(Diacetoxyiodo)benzene	Iodobenzene diacetate Phenyliodo diacetate Iodosobenzene diacetate Phenyliodine(III) diacetate	DIB, IBD PIDA IBDA
PhI(OCOCF <sub>3</sub> ) <sub>2</sub>	[Bis(trifluoroacetoxy) iodo]benzene	Iodobenzene bis(trifluoroacetate)	BTI
PhI(OH)OTs	[Hydroxy(4-methylphenyl sulfonyloxy)iodo]benzene	Phenyliodo bis(trifluoroacetate) Phenyliodine(III) bis(trifluoroacetate) [Hydroxy(tosyloxy)iodo] benzene	PIFA HTIB, HTI
PhIO	Iodosylbenzene	Koser's reagent Iodosobenzene	IDB
	1-Hydroxy-1H-1 $\lambda^3$ - benzo[d][1,2]iodoxol-3-one	2-Iodosobenzoic acid	IBA
Ph <sub>2</sub> ICl	Diphenyliodonium chloride or chloro(diphenyl)- $\lambda^3$ -iodane	2-Iodosylbenzoic acid <i>o</i> -Iodosobenzoic acid 1-Hydroxy-1,2-benziodoxol-3-(1H)- one	DPI
PhINTs	[N-(4-Methylphenylsulfonyl) imino]phenyl- $\lambda^3$ -iodane	Chlorodiphenyliodonium	None
IF <sub>5</sub>	Iodine pentafluoride or pentafluoro- $\lambda^5$ -iodane	( <i>N</i> -Tosylimino)phenyliodinane	None
HIO <sub>3</sub>	Iodic acid	Iodine(V) fluoride Iodic fluoride	None
PhIO <sub>2</sub>	Iodylbenzene	Iodic(V) acid Iodoxybenzene	None
	1-Hydroxy-1-oxo-1H-1 $\lambda^5$ - benzo[d][1,2]iodoxol-3-one	2-Iodoxybenzoic acid 2-Iodylbenzoic acid <i>o</i> -Iodoxybenzoic acid	IBX
	1,1,1-Triacetoxy-1H-1 $\lambda^5$ - benzo[d][1,2]iodoxol-3-one	Dess–Martin periodinane	DMP
IF <sub>7</sub>	Iodine heptafluoride or heptafluoro- $\lambda^7$ -iodane	Iodine(VII) fluoride Heptafluoroiodine	None
HIO <sub>4</sub>	Periodic acid	Iodic(VII) acid	None

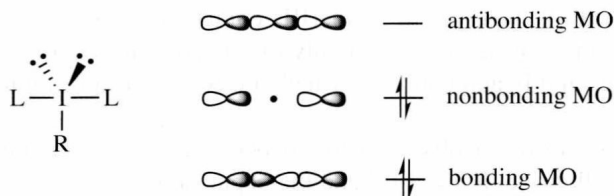


X = Me,  $\text{CF}_3$  or  $2\text{X} = \text{O}$ ;  
 Y = OH, OAc,  $\text{N}_3$ , CN, etc.; Z = H, Ac, etc.

**Figure 1.2** Common classes of organoiodine(III) compounds.



**Figure 1.3** Common classes of organoiodine(V) compounds.

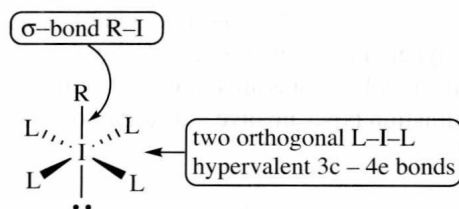


**Figure 1.4** Molecular orbital description of the three-center-four-electron bond in hypervalent iodine(III) molecules  $RIL_2$ .

The idea of a three-center-four-electron (3c-4e) bond was independently proposed by G. C. Pimentel [130] and R. E. Rundle [131] in 1951 on the basis of molecular orbital theory. According to the fundamental description of the 3c-4e bond for  $L-X-L$ , one pair of bonding electrons is delocalized to the two ligands  $L$ , resulting in the charge distribution of almost  $-0.5$  on each ligand and  $+1.0$  on the central atom  $X$ . In iodine(III) molecules  $RIL_2$ , the interaction of the filled  $5p$  orbital of the central iodine atom and the half-filled orbitals of the two ligands  $L$  *trans* to each other leads to formation of three molecular orbitals: bonding, nonbonding and antibonding (Figure 1.4). Because the highest occupied molecular orbital (HOMO) contains a node at the central iodine, the hypervalent bonds show a highly polarized nature; hence, more electronegative atoms tend to occupy the axial positions formed by the interaction of the orbitals of three collinear atoms. The carbon substituent  $R$  is bound by a normal covalent bond and the overall geometry of molecule  $RIL_2$  is a distorted trigonal bipyramid with two heteroatom ligands  $L$  occupying the apical positions and the least electronegative carbon ligand  $R$  and both electron pairs reside in equatorial positions.

The bonding in iodine(V) compounds,  $RIL_4$ , with a square bipyramidal structure may be described in terms of a normal covalent bond between iodine and the organic group  $R$  in an apical position and two orthogonal, hypervalent 3c-4e bonds, accommodating four ligands  $L$ . The carbon substituent  $R$  and unshared electron pair in this case should occupy the apical positions with the electronegative ligands  $L$  residing at equatorial positions (Figure 1.5).

Several theoretical computational studies concerning bonding, structure and reactivity of hypervalent iodine compounds were published in the 1990s and 2000s [132–137]. In particular, Reed and Schleyer provided a general theoretical description of chemical bonding in hypervalent molecules in terms of the dominance of ionic bonding and negative hyperconjugation over  $d$ -orbital participation [132]. The simple, qualitative bonding concepts for hypervalent molecules developed in this work supersede the inaccurate and misleading  $dsp^3$  and  $d^2sp^3$  models. It has been recognized that there are fundamental similarities in bonding, structure and reactivity of hypervalent  $\lambda^3$ - and  $\lambda^5$ -iodanes with organometallic compounds. In fact, it has been stated in some theoretical studies that, similar to the heavy main group elements, hypervalent bonding commonly occurs in transition metal complexes and the 3c-4e bond is particularly important in the structure of transition metal hydrides [138–142]. The important and well known in transition metal complexes, effect of *trans*



**Figure 1.5** Bonding in hypervalent iodine(V) molecules.

influence [136] is also typical of hypervalent iodine(III) compounds (Section 1.4.2) [135, 136, 143]. The reactions of hypervalent iodine reagents are commonly discussed in terms of oxidative addition, reductive elimination, ligand exchange and ligand coupling, which are typical of transition metal chemistry (Section 1.5).

Typical structures of iodine(VII) involve a distorted octahedral configuration **6** about iodine in most periodates [144] and the oxyfluoride, IOF<sub>5</sub> [145] and the heptacoordinated, pentagonal bipyramidal species **7** for IF<sub>7</sub> and the IOF<sub>6</sub><sup>−</sup> anion (Figure 1.1) [146, 147]. The pentagonal bipyramidal structure **7** has been described as two covalent, collinear, axial bonds between iodine and the ligands in the apical positions and a coplanar, hypervalent 6c-10e bond system for the five equatorial bonds [146].

## 1.4 General Structural Features

The structural aspects of polyvalent iodine compounds were previously summarized in several books and reviews [20, 30, 32, 127]. In general, the molecular structure of λ<sup>3</sup>- and λ<sup>5</sup>-iodanes is predetermined by the nature of hypervalent bonding discussed in Section 1.3. The key structural features of the hypervalent organoiodine compounds available from numerous X-ray data may be summarized as follows:

1. λ<sup>3</sup>-Iodanes RIX<sub>2</sub> (R = C-ligand, X = heteroatom ligands) have an approximately T-shaped structure with a collinear arrangement of the most electronegative ligands X. Including the nonbonding electron pairs, the geometry about iodine is a distorted trigonal bipyramid with the most electronegative groups occupying the apical positions, while the least electronegative C-ligand R and both electron pairs reside in an equatorial position.
2. The I–C bond lengths in iodonium salts R<sub>2</sub>I<sup>+</sup> X<sup>−</sup> and λ<sup>3</sup>-iodanes RIX<sub>2</sub> are approximately equal to the sum of the covalent radii of iodine and carbon, ranging generally from 2.00 to 2.10 Å.
3. Iodonium salts R<sub>2</sub>I<sup>+</sup> X<sup>−</sup> generally have a typical distance between iodine and the nearest anion X<sup>−</sup> of 2.6–2.8 Å and in principle can be considered as ionic compounds with pseudo-tetrahedral geometry about the central iodine atom. However, with consideration of the anionic part of the molecule, the overall experimentally determined geometry is distorted T-shaped structure similar to the λ<sup>3</sup>-iodanes RIX<sub>2</sub>.
4. For λ<sup>3</sup>-iodanes RI(X)Y with two heteroatom ligands X and Y of the same electronegativity, both I–X and I–Y bonds are longer than the sum of the appropriate covalent radii, but shorter than purely ionic bonds. For example, the I–Cl bond lengths in PhICl<sub>2</sub> are 2.45 Å [148] and the I–O bond lengths in PhI(OAc)<sub>2</sub> are 2.15–2.16 Å [149], while the sum of the covalent radii of I and O is 1.99 Å. When heteroatom ligands X and Y have different electronegativities, the *trans* influence of ligands has a strong effect on the structure, stability and reactivity of λ<sup>3</sup>-iodanes RI(X)Y (Section 1.4.2) [135].
5. Various coordination types have been reported for the organoiodine(V) compounds. Depending on the ligands and taking into account secondary bonding, the overall observed geometry for the structural types **4** and **5** (Figure 1.1) can be pseudo-trigonal-bipyramidal, square bipyramidal and pseudooctahedral.
6. Intramolecular positional isomerization (Berry pseudorotation) resulting in an exchange between the apical and the equatorial ligands occurs rapidly in both λ<sup>3</sup>- and λ<sup>5</sup>-iodanes. This process is important in explaining the mechanisms of hypervalent iodine reactions (Section 1.5).
7. Only inorganic compounds with O- or F-ligands are known for iodine(VII) structural types **6** and **7** (Figure 1.1). Typical iodine(VII) coordination types involve a distorted octahedral configuration and pentagonal bipyramidal species.

Owing to a highly polarized character of hypervalent bond, noncovalent attractive interactions of a predominantly electrostatic nature are extremely important in the structural chemistry of hypervalent iodine

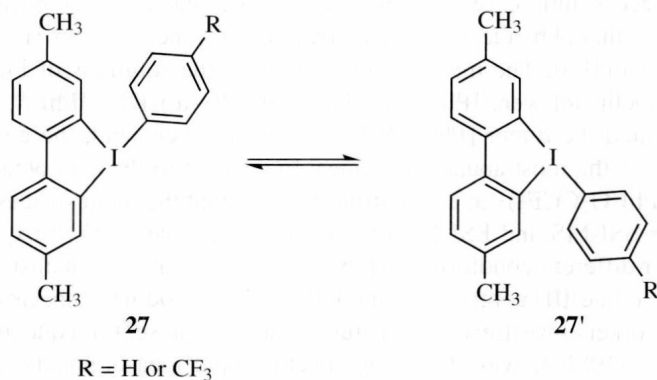


compounds. Such attractive interactions are commonly called secondary bonds. Similarly to hydrogen bonds, secondary bonds involving heavier atoms have strong electrostatic components and show directional preferences [150, 151]. Intermolecular secondary bonding in hypervalent iodine compounds is responsible for crystal packing in the solid state and for the self-assembly of individual molecules into complex supramolecular structures in the solid state and in solution [152, 153]. Intramolecular secondary bonding is commonly observed in the  $\lambda^3$ - and  $\lambda^5$ -aryliodanes, which have a sulfonyl or a carbonyl structural fragment in the *ortho*-position of the phenyl ring [154–159]. The redirection of secondary bonding from intermolecular to intramolecular mode due to the presence of an appropriate *ortho*-substituent leads to a partial disruption of the polymeric network and enhances solubility of a hypervalent iodine compound [154, 155].

### 1.4.1 Experimental Structural Studies

Numerous X-ray crystal structures have been reported for all main classes of organic polyvalent iodine compounds and the results of these studies are overviewed in the appropriate sections of Chapter 2. Typical coordination patterns in various organic derivatives of iodine(III) in the solid state with consideration of primary and secondary bonding were summarized in 1986 by Sawyer and coworkers [160] and have been updated in several more recent publications [153, 161–165]. Structural features of organic iodine(V) compounds have been discussed in the older papers of Martin and coauthors [166, 167] and in numerous recent publications on IBX and related  $\lambda^5$ -iodanes [155–159, 168–174]. Several general areas of structural research on hypervalent organoiodine compounds have attracted especially active interest. These areas, in particular, include the preparation and structural study of complexes of hypervalent iodine compounds with crown ethers [175–179] or nitrogen ligands [180–182], self-assembly of hypervalent iodine compounds into various supramolecular structures [152, 153, 164, 183, 184] and the intramolecular secondary bonding in *ortho*-substituted aryliodine(V) and aryliodine(III) derivatives [154–159, 168–171, 173, 174, 185–188].

Several important spectroscopic structural studies of polyvalent iodine compounds in solution have been published [108–112, 189]. Reich and Cooperman reported low-temperature NMR study of triaryl- $\lambda^3$ -iodanes **27** (Scheme 1.1), which demonstrated that these compounds have a nonsymmetrical planar orientation of iodine–carbon bonds and that the barrier to unimolecular degenerate isomerization between **27** and **27'** is greater than 15 kcal mol<sup>−1</sup>. The exact mechanism of this degenerate isomerization is unknown; both pseudorotation on iodine(III) and intermolecular ligand exchange may account for the isomerization of these compounds [189].



**Scheme 1.1** Degenerate isomerization of triaryl- $\lambda^3$ -iodanes **27** in solution.