

Introduction to Inorganic Rings and Polymers

1.1 CLASSIFICATION

Ring systems represent a very important branch of organic chemistry. Benzene is perhaps the pre-eminent example and provides the benchmark for the so-called aromatic character of cyclic systems. Experimental and theoretical studies of this unsaturated compound have provided important insights into delocalised chemical bonding, and also an understanding of the substitution patterns. Cycloalkanes are another prominent class of organic compounds. These saturated ring systems form a homologous series, $(\text{CH}_2)_n$ ($n = 3$ to > 30), known as alicyclics.

Materials that are constructed from organic polymers such as polyethylene, polystyrene, polyisoprene (natural rubber and a synthetic elastomer) and poly(vinyl chloride) are common features of our daily lives. Most of these and related organic polymers are generated from acyclic precursors by free radical, anionic, cationic or organometallic polymerisation processes or by condensation reactions. Cyclic precursors are rarely used for the production of organic polymers.

The replacement of one or more carbon atoms in a homocyclic organic system by another p-block element gives rise to heterocycles. Common examples include the unsaturated rings thiophene, $\text{C}_4\text{H}_4\text{S}$, and pyridine, $\text{C}_5\text{H}_5\text{N}$, and the saturated heterocycle tetrahydrofuran, $\text{C}_4\text{H}_8\text{O}$. This process of heteroatom substitution can be continued with the replacement of two or more carbons by the same (or different) p-block elements. The study of this class of compounds comprises the field of heterocyclic chemistry. Since approximately half of known organic compounds contain at least one heterocyclic component, this branch of organic chemistry is vast. The extension of this heteroatom

substitution process to the complete replacement of all carbon atoms in a ring system by other p-block elements produces inorganic heterocycles which, together with the polymers derived from them, are the subject of this book. A useful classification of inorganic ring systems can be found in the article by Haiduc in the *Encyclopedia of Inorganic Chemistry*.¹

A quintessential inorganic ring system is elemental sulfur, which, in its thermodynamically stable elemental form, exists as an eight-membered ring, cyclo-S₈. In common with cycloalkanes, homocyclic sulfur rings cyclo-S_n can range in size from $n=6$ to *ca* 24 (Sections 6.1 and 12.1.1). Another type of saturated inorganic ring system that forms an extensive homologous series are the cyclosilanes, (R₂Si)_n ($n=3-35$) (Sections 6.1 and 10.1.1). An intriguing example of an inorganic homocycle is the arsenic-based drug Salvarsan, which, as the forerunner of chemotherapy, was used in the early part of the 20th century for the treatment of syphilis. Recently, Salvarsan was shown to consist primarily of a mixture of three- and five-membered homocyclic arsenic rings, (RAs)_n ($n=3, 5$; R = 3-NH₂-4-OHC₆H₃) (Sections 3.2 and 11.3.2).

1.2 HISTORICAL BACKGROUND

The first inorganic heterocycle, the cyclotriphosphazene (NPCl₂)₃, was described in 1834 and the second example, tetrasulfur tetranitride, S₄N₄, was reported a year later, but it was over century before the structures of these fascinating molecules were shown to be comprised of a six-membered ring and a folded cage structure, respectively. These structural determinations raised fundamental questions about the nature of the bonding in inorganic heterocycles, which provided a focus for much of the early work on inorganic ring systems. Borazine, B₃N₃H₆, was discovered in 1926. Because of its isoelectronic relationship to C₆H₆, borazine is sometimes referred to as 'inorganic benzene', but the debate over the aromaticity of this six-membered ring continues even today (Section 4.1.2.1). Interestingly, an extensive homologous series exists for the cyclophosphazenes, (NPX₂)_n (X = Cl, F; $n=3-40$) (Sections 6.2.2 and 11.4.2), whereas ring systems other than the six-membered borazines are the exception for boron–nitrogen systems. The reasons for this different behaviour will be discussed in later chapters.

1.3 INDUSTRIAL APPLICATIONS

Industrial interest in inorganic ring systems was stimulated in the 1940s by the discovery that cyclosiloxanes, (R₂SiO)_n ($n=3, 4$), are important intermediates in the manufacture of silicone (siloxane) polymers, (R₂SiO)_n (Section 10.6). Today, these inorganic polymers are made on a massive scale annually because of their multifarious uses in modern society as oils, greases, rubbers, polishes, coatings and insulating materials. Polysilanes, (R₂Si)_n, are of interest as ceramic precursors and in the application of microlithography in the electronics industry (Section 10.1.4.1). Phosphazene polymers, (NPR₂)_n (R = HNMe, OCH₂CF₃, OC₆H₅), have many desirable properties that have led to a variety

of significant applications, *e.g.* as water repellents, non-flammable fibres, foams, fuel pipes and metal ion conductors in batteries (Section 11.4.3). However, the widespread use of phosphazene polymers has been hampered by their high cost relative to that of silicones. In addition to their importance as precursors to inorganic polymers, more recent applications of inorganic ring systems have focused on their use as sources of functional inorganic materials such as semiconductors and ceramics.

1.4 SCOPE AND LIMITATIONS

In this book, the focus is on *monocyclic* inorganic ring systems and the inorganic polymers that, in many cases, are derived from them. Catenated species and related linear oligomers are discussed when their formation or structures are connected with either the corresponding monocyclic systems or the polymers derived from them. Bicyclic or polycyclic arrangements will be considered when they are closely related to those of monocyclic systems as a result of a transannular interaction or structural isomerism, *e.g.* in a discussion of the structural trends of polychalcogen cations (Section 12.3) and anions (Section 12.4). Inorganic heterocycles that are more accurately described as coordination complexes of chelating inorganic ligands are included only when they are directly related to an inorganic homocycle or heterocycle by the replacement of one p-block element by a more metallic p-block element, *e.g.* in a discussion of the applications of p-block metal complexes of the inorganic ligand $[\text{EPR}_2\text{NPR}_2\text{E}]^-$ ($\text{E} = \text{S}, \text{Se}, \text{Te}$) as single-source precursors for the production of thin films of semiconducting metal chalcogenides.

1.5 ORGANISATION

The first six chapters (Chapters 2–7) are intended to provide an introduction to the field of inorganic ring systems. We begin in Chapter 2 by discussing the various methods that are available for the synthesis of inorganic heterocycles. This is followed in Chapter 3 by consideration of the techniques that are most commonly used for their characterisation. Chapter 4 deals with concepts related to the structures and bonding of inorganic ring systems in the context of electron delocalisation (aromaticity). The role of frontier orbitals in the formation and reactions of inorganic ring systems is also stressed in that chapter. The subsequent three chapters (5–7) consider (a) paramagnetic systems with unique magnetic or conducting properties, (b) inorganic macrocycles and their uses in host–guest chemistry and (c) inorganic ring systems as ligands in metal complexes. This discussion leads naturally in Chapter 8 to an account of the methods used to synthesise inorganic polymers, since the most commonly used approach to these macromolecules is ring-opening polymerisation. This final introductory chapter also gives details of the most common techniques used to characterise the structures and properties of inorganic polymers.

After this introductory background to general concepts related to the chemistry of inorganic rings and polymers of the p-block elements, the second half of

the book is comprised of four chapters that discuss specific ring systems and polymers involving the elements of groups 13–16 in considerable detail. The material chosen for inclusion in these chapters is intended to reinforce, with examples, the most important concepts introduced in Chapters 2–8. Although they are not intended to be comprehensive, these chapters do include early seminal contributions to the field and also the most important recent advances up to the middle of 2008. The applications of inorganic ring systems as precursors to functional inorganic materials such as semiconducting thin films, nanoparticles, quantum dots and ceramics are included in these chapters. Group 17 is not included because the halogens generally do not form ring systems involving two-electron, two-centre bonds. The fascinating structural chemistry of polyiodides, which includes a multifarious array of linear and polycyclic architectures involving weak I–I interactions, is covered in a recent comprehensive review.²

1.6 NOMENCLATURE

The nomenclature of inorganic ring systems presents a number of significant challenges that have been discussed at length in various publications.³ Interested readers are directed to the most recent IUPAC recommendations published in 2005,⁴ which are intended to be the definitive guide to the topic. Since the recommended names for many inorganic ring systems are long and unwieldy, in this book we refer to inorganic ring systems by the names that are commonly used in the literature. It is hoped that the copious use of structural drawings and Figures to depict their structures will minimise any ambiguities that may arise from this pragmatic approach.

1.7 BIBLIOGRAPHY

A selection of inorganic and organometallic textbooks that give a good background discussion of various aspects of inorganic ring systems is given at the end of this introduction. This book is intended to serve as a supplement to those general inorganic chemistry texts in senior undergraduate and graduate courses. In order to minimise unnecessary duplication of background material in Chapters 9–12, references are made to the appropriate sections of these textbooks when the topics are covered in some depth in those sources. More specialised reviews and extensive leading references to the primary literature are included at the end of each individual chapter.

This bibliography also includes a list of recent monographs that deal specifically with ‘Inorganic Ring Systems’, ‘Inorganic Polymers’ or ‘Cluster Molecules of the p-Block Elements’. There are several recent books that deal specifically with inorganic polymers, but the latest comprehensive treatment of inorganic ring systems is the 1992 two-volume set edited by Studel. There is no text that makes the connection between the fundamental aspects of the chemistry of inorganic homo- and heterocycles and their applications as functional inorganic materials such as polymers, ceramics and semiconductors for the electronics industries.

REFERENCES

1. I. Haiduc, Inorganic ring systems, in: *Encyclopedia of Inorganic Chemistry*, ed. R. B. King, 2nd edn., Wiley, Chichester, 2005, pp. 2028–2055.
2. P. H. Svensson and L. Kloo, Synthesis, structure and bonding in polyiodide and metal iodide–iodine systems, *Chem. Rev.*, 2003, **103**, 1649.
3. I. Haiduc, Comments on the nomenclature of inorganic ring systems, in *The Chemistry of Inorganic Ring Systems*, ed. R. Steudel, Elsevier, Amsterdam, 1992, pp. 451–477, and references cited therein.
4. N. G. Connelly, T. Damhus, R. M. Hartshorn and A. T. Hutton (eds), *Nomenclature of Inorganic Chemistry; IUPAC Recommendations 2005*, Royal Society of Chemistry, Cambridge, 2005.

General Texts in Inorganic and Organometallic Chemistry

- N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd edn., Butterworth-Heinemann, Oxford, 1998.
- N. Wiberg and B. J. Aylett (eds), *Holleman–Wiberg Inorganic Chemistry*, Academic Press, London, 2001.
- C. E. Housecroft and A. G. Sharpe, *Inorganic Chemistry*, 2nd edn., Pearson Education, Harlow, 2005.
- C. Elschenbroich, *Organometallics*, 3rd edn., Wiley-VCH, Weinheim, 2005.

Inorganic Rings and Chains

- I. Haiduc, *The Chemistry of Inorganic Ring Systems*, Wiley-Interscience, London, 1970.
- D. A. Armitage, *Inorganic Rings and Chains*, Edward Arnold, London, 1972.
- A. L. Rheingold (ed.), *Homoatomic Rings Chains and Macromolecules of Main-group Elements*, Elsevier, Amsterdam, 1977.
- H. G. Heal, *The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus*, Academic Press, London, 1980.
- F. L. Boschke (ed.), *Inorganic Ring Systems*, Topics in Current Chem., Vol. **102**, 1982.
- A. H. Cowley (ed.), *Rings, Clusters and Polymers of the Main Group Elements*, ACS Symposium Series, Vol. **232**, 1983.
- I. Haiduc and D. B. Sowerby (eds), *The Chemistry of Inorganic Homo- and Heterocycles*, Vols 1 and 2, Academic Press, London, 1987.
- J. D. Woollins, *Non-metal Rings, Cages and Clusters*, Wiley, Chichester, 1988.
- H. W. Roesky, *Rings, Clusters and Polymers of Main Group and Transition Elements*, Elsevier, Amsterdam, 1989.
- R. Steudel (ed.), *The Chemistry of Inorganic Ring Systems*, Vols 1 and 2, Elsevier, Amsterdam, 1992.

T. Chivers, *A Guide to Chalcogen–Nitrogen Chemistry*, World Scientific, Singapore, 2005.

Inorganic Polymers

- R. D. Archer, *Inorganic and Organometallic Polymers*, Wiley, New York, 2001.
- H. R. Allcock, *Chemistry and Applications of Polyphosphazenes*, Wiley-Interscience, New York, 2003.
- M. Gleria and R. De Jaeger, *Phosphazenes: a Worldwide Insight*, Nova Publishers, Hauppauge, NY, 2004.
- V. Chandrasekhar, *Inorganic and Organometallic Polymers*, Springer-Verlag, Berlin, 2005.
- J. E. Mark, H. R. Allcock and R. West, *Inorganic Polymers*, 2nd edn., Oxford University Press, Toronto, 2005.

Inorganic Clusters

- C. E. Housecroft, *Cluster Molecules of the p-Block Elements*, Oxford University Press, Oxford, 1994.
- M. Driess and H. Nöth (eds), *Molecular Clusters of the Main Group Elements*, Wiley-VCH, Weinheim, 2004.