Group Theory and Chemistry

DAVID M. BISHOP

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DAVID M. BISHOP
PROFESSOR OF CHEMISTRY, UNIVERSITY OF OTTAWA

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Preface

THIS book is written for chemistry students who wish to understand how group theory is applied to chemical problems. Usually the major obstacle a chemist finds with the subject of this book is the mathematics which is involved; consequently, I have tried to spell out all the relevant mathematics in some detail in appendices to each chapter. The book can then be read either as an introduction, dealing with general concepts (ignoring the appendices), or as a fairly comprehensive description of the subject (including the appendices). The reader is recommended to use the book first without the appendices and then, having grasped the broad outlines, read it a second time with the appendices.

The subject material is suitable for a senior undergraduate course or for a first-year graduate course and could be covered in 15 lectures (without the appendices) or in 21 lectures (with the appendices).

The best advice about reading a book of this nature was probably that given by George Chrystal in the preface to his book *Algebra:*

> Every mathematical book that is worth reading must be read "backwards and forwards", if I may use the expression. I would modify Lagrange's advice a little and say, "Go on, but often return to strengthen your faith". When you come on a hard or dreary passage, pass it over, and come back to it after you have seen its importance or found the need for it further on.

Finally, a word of encouragement to those who are frightened by mathematics. The mathematics involved in actually applying, as opposed to deriving, group theoretical formulae is quite trivial. It involves little more than adding and multiplying. It is in fact possible to make the applications, by filling in the necessary formulae in a routine way, without even understanding where the formulae have come from. I do not, however, advocate this practice.

London D. M. B.
November 1972

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I acknowledge with thanks permission to reproduce the following figures:

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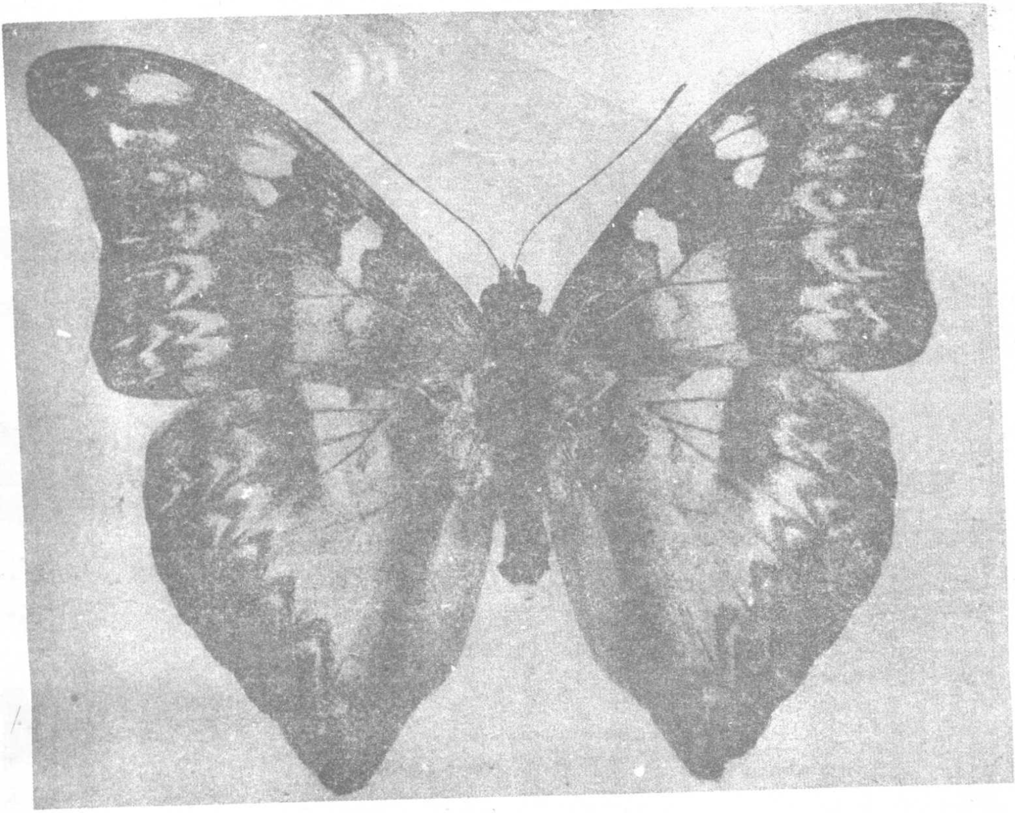
I am similarly grateful to Dr. D. S. Schonland for permission to reproduce, in Appendix I, the character tables of his book *Molecular symmetry* (Van Nostrand Co. Ltd.).

Last, I would like to thank Mrs. M. R. Robertson for her immaculate typing.

List of symbols

R	symmetry element
$\boldsymbol{R}$	symmetry operation
$D(\boldsymbol{R})$	matrix representing $\boldsymbol{R}$
$D_{ij}(\boldsymbol{R})$	element in the ith row, jth column of $D(\boldsymbol{R})$
$\boldsymbol{O}_{\boldsymbol{R}}$	transformation operator corresponding to $\boldsymbol{R}$
A	matrix, elements are displayed between two pairs of vertical lines
A_{ij}	element in the ith row, jth column of A
$\mathscr{A}_{ij}$	cofactor of A_{ij} in $\det(A)$
$\det(A)$	determinant of A
$\mathrm{Trace}(A)$	trace of A
A^*	conjugate complex of A
$\tilde{A}$	transpose of A
A^{+}	adjoint of A
A^{-1}	inverse of A
X	matrix
x_i	ith column of X
x_{ij}	element in the ith row, jth column of X
E	identity matrix
0	null matrix
$\mathscr{G}$	point group
g	order of a group (number of elements in a group)
g_i	number of elements in the ith class of a group
δ_{ij}	Kronecker delta (equals 0 if $i \neq j$, equals 1 if $i = j$)
x_1, x_2, x_3	Cartesian coordinates of a point
Γ	a representation of a point group
Γ^{μ}	the μth representation of a point group
$D^{\mu}(\boldsymbol{R})$	the matrix representing $\boldsymbol{R}$ in Γ^{μ}
$D^{\mu}_{ij}(\boldsymbol{R})$	the matrix element in the ith row and jth column of $D^{\mu}(\boldsymbol{R})$
n_{μ}	the dimension of Γ^{μ} or the order of $D^{\mu}(\boldsymbol{R})$
$\chi(\boldsymbol{R})$	the character of $\boldsymbol{R}$ in Γ
$\chi^{\mu}(\boldsymbol{R})$	the character of $\boldsymbol{R}$ in Γ^{μ}
$\boldsymbol{P}^{\mu}(\boldsymbol{R})$	the projection operator $\sum_{\boldsymbol{R}} \chi^{\mu}(\boldsymbol{R})^* \boldsymbol{O}_{\boldsymbol{R}}$
$\boldsymbol{P}^{\mu}_{ij}(\boldsymbol{R})$	the projection operator $\sum_{\boldsymbol{R}} D^{\mu}_{ij}(\boldsymbol{R})^* \boldsymbol{O}_{\boldsymbol{R}}$
a_{μ}	the number of times Γ^{μ} occurs in Γ
k	the number of classes in a group
$D^{\mathrm{reg}}(\boldsymbol{R})$	the matrix representing $\boldsymbol{R}$ in the regular representation Γ^{reg}
$\boldsymbol{C}_i$	any operation of the ith class of a point group
$\boldsymbol{R}^m_j$	the jth operation of the mth class of a point group
$\oplus$	symbol linking the irreducible components of a reducible representation
$\otimes$	symbol linking two representations in a direct product representation

E_ν	νth energy level
ψ^ν	a wavefunction associated with E_ν
X	a set of coordinates for a number of particles
X_{nuc}	a set of coordinates for a number of nuclei
X_{el}	a set of coordinates for a number of electrons



(a)

(b)

FIG. 1-2.1. (a) Cymothoe aloatia; (b) primrose.

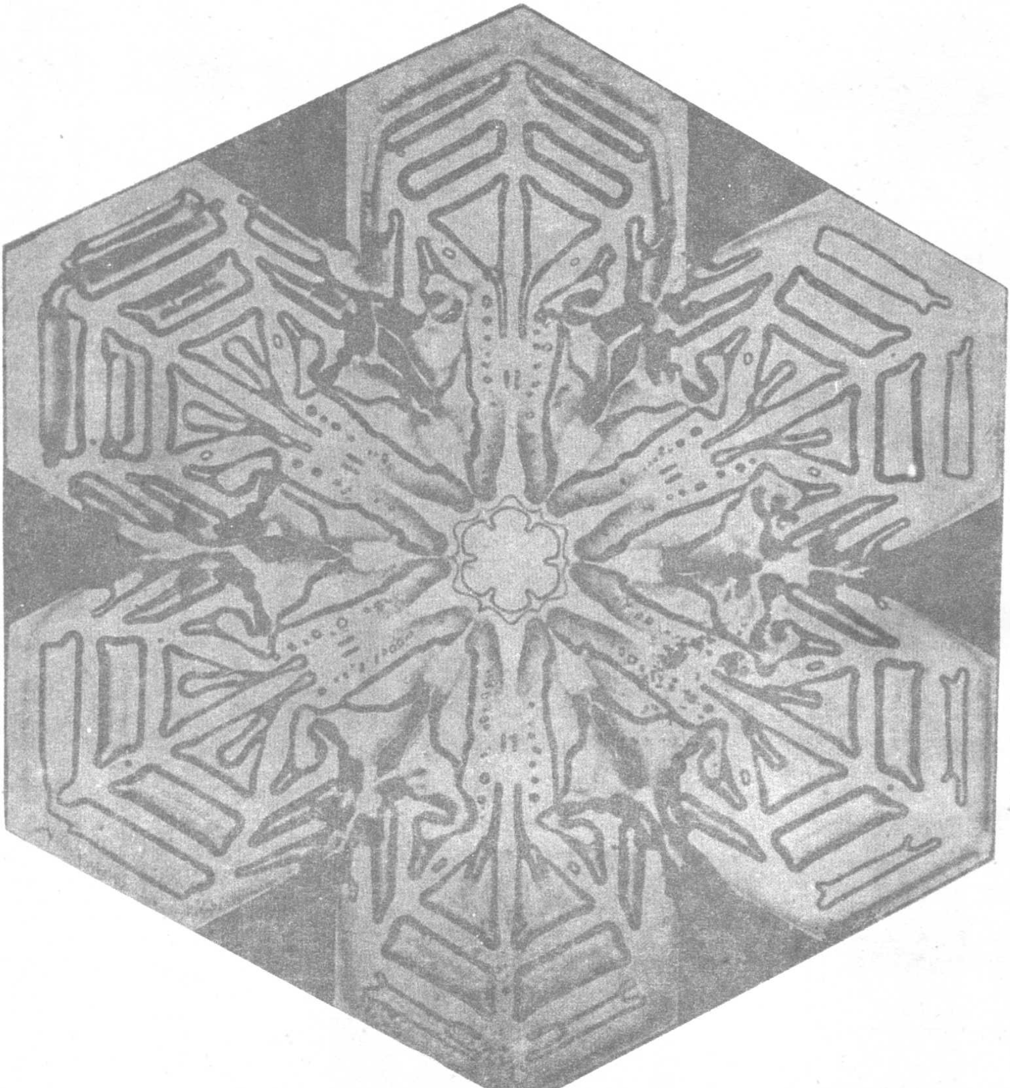


FIG. 1-2.1. (c) ice crystal.

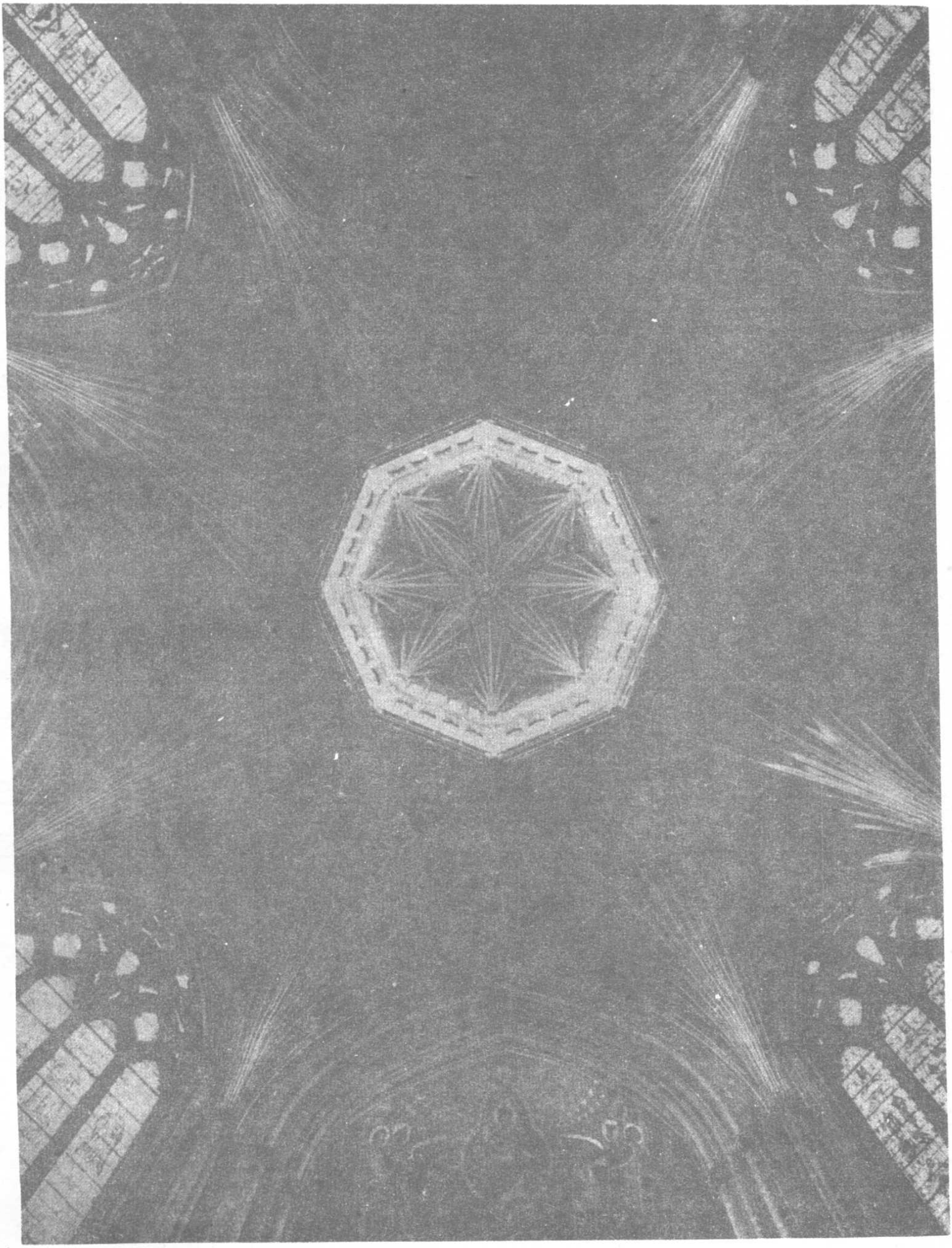


FIG. 1-2.3. The octagonal ceiling in Ely Cathedral.

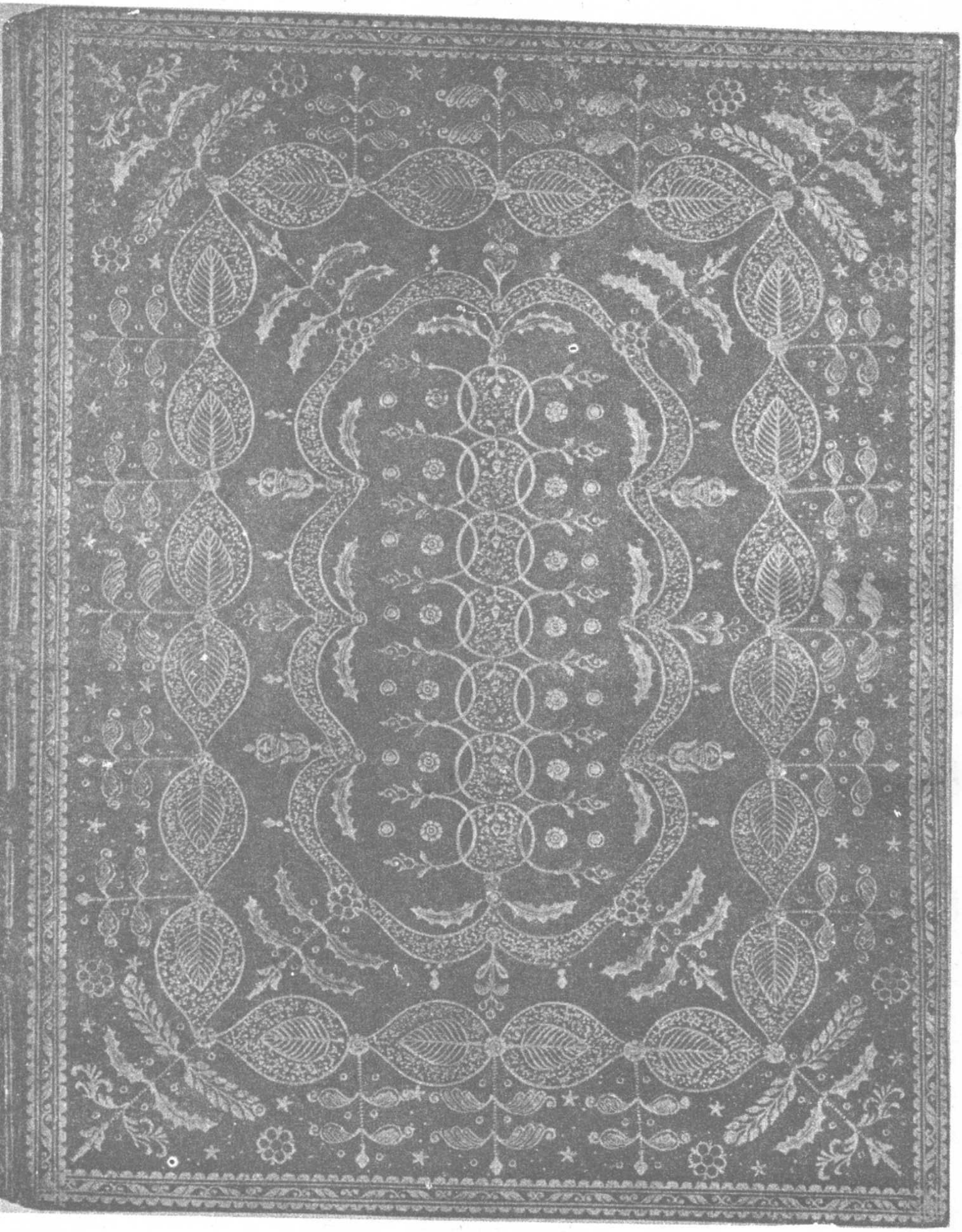


FIG. 1-2.5. An example of Scottish bookbinding, circa 1750.

Contents

1. Symmetry

1-1. Introduction

IN everyday language we use the word *symmetry* in one of two ways and correspondingly the Oxford English Dictionary gives the following two definitions:

(1) Mutual relation of the parts of something in respect of magnitude and position; relative measurement and arrangement of parts; proportion.

(2) Due or just proportion; harmony of parts with each other and the whole; fitting, regular, or balanced arrangement and relation of parts or elements; the condition or quality of being well proportioned or well balanced.

The first definition of the word has a more scientific ring to it than the second, the second being related to some extent to the rather more nebulous concept of beauty, for example John Bulwer wrote in 1650: 'True and native beauty consists in the just composure and symetrie of the parts of the body'.† It is nonetheless interesting that when we go deeper into the scientific meaning of symmetry we find that the underlying mathematics involved has itself a beauty and elegance which could well be described by the second definition.

In this chapter we will first look at symmetry as it occurs in everyday life and then consider its specific role in chemistry. We will end the chapter by giving a historical sketch of the development of the mathematics which is used in making use of symmetry in chemistry.

1-2. Symmetry and everyday life

The ubiquitous role of symmetry in everyday life has been neatly summarized by James Newman in the following way:

> Symmetry establishes a ridiculous and wonderful cousinship between objects, phenomena, and theories outwardly unrelated: terrestial magnetism, women's veils, polarized light, natural selection, the theory of groups, invariants and transformations, the work habits of bees in the hive, the structure of space, vase designs, quantum physics, scarabs, flower petals,

† This quotation comes from a book with the extraordinary title, *Anthropometamorphosis: Man Transform'd; or the Artificial Changeling. Historically presented, in the mad and cruel Gallantry, foolish Bravery, ridiculous Beauty, filthy finenesse, and loathsome Loveliness of most Nations, fashioning and altering their Bodies from the Mould intended by Nature. With a Vindication of the Regular Beauty and Honesty of Nature. And an Appendix of the Pedigree of the English Gallant.*

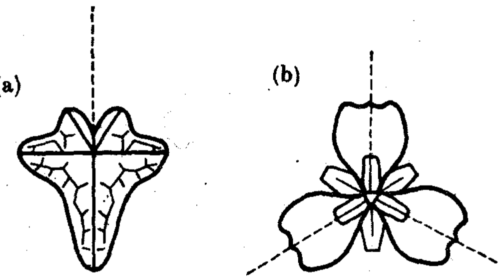


FIG. 1-2.2. (a) Ivy leaf; (b) iris. Dotted lines show planes of symmetry perpendicular to the page.

X-ray interference patterns, cell division in sea urchins, equilibrium positions in crystals, Romanesque cathedrals, snowflakes, music, the theory of relativity.†

In nature we find countless examples of symmetry and in Fig. 1-2.1 we show some rather beautiful examples from the animal, vegetable, and mineral kingdoms. Externally, most animals have bilateral symmetry that is to say they contain a single *plane of symmetry;* such a plane bisects every straight line joining a pair of corresponding points. This is the same thing as saying that the plane divides the object into two parts which are mirror images of each other. In Fig. 1-2.2 it is seen that the ivy leaf and iris have, perpendicular to the plane of the page, one and three planes of symmetry respectively. Actually, the most frequent number of planes of symmetry in flowers is five. Anyone interested in the predominance of bilateral symmetry in the animal world, with its corollary of left and right handedness, is recommended to read *The ambidextrous universe.*‡ In the iris we also notice that there is a three-fold *axis of symmetry*, that is, if we rotate the flower by $2\pi/3$ radians about the axis perpendicular to the page and running down the centre of the flower, then we cannot tell that it has been moved. Similarly, the ice crystal in Fig. 1-2.1 has a six-fold axis of symmetry: a $2\pi/6$ rotation leaves it apparently unmoved.

Because of its basic aesthetic appeal (regularity, pleasing proportions, periodicity, harmonious arrangement) symmetry has, since time immemorial, been used in art. Probably the first example a child experiences of the beauty of symmetry is in playing with a kaleidoscope. More erudite examples occur in: poetry, for example the *abccba* rhyming sequence in many poems; architecture, for example the octagonal ceiling in Ely Cathedral (see Fig. 1-2.3); music, perhaps the most astute use of symmetry in art is a two part piece of music which is sometimes

† *The world of mathematics*, vol. 1, p. 669, Allen and Unwin, London (1960).
‡ M. Gardner, *The ambidextrous universe*, Allen Lane, Penguin Press, London (1967).