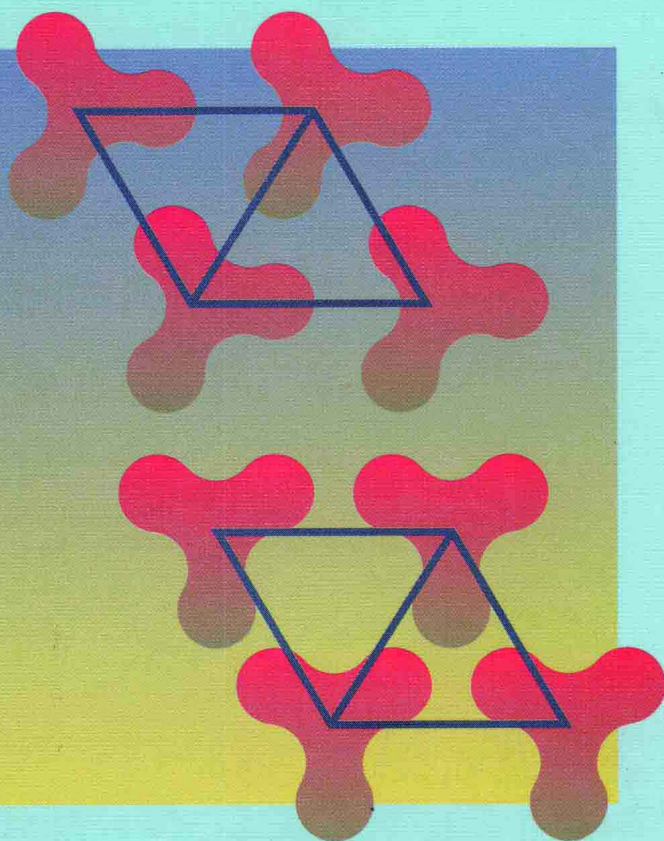


Jack D. Dunitz

X-Ray Analysis and the Structure of Organic Molecules



江苏工业学院图书馆
藏书章

X-Ray Analysis and the Structure of Organic Molecules



© Verlag Helvetica Chimica Acta, CH-4010 Basel (Switzerland), 1995

Distribution

VCH, P.O. Box 101161, D-69451 Weinheim (Federal Republic of Germany)

Switzerland: VCH, P.O. Box, CH-4020 Basel (Switzerland)

United Kingdom and Ireland: VCH (UK) Ltd., 8 Wellington Court, Wellington Street, Cambridge CB1 1HZ (England)

USA and Canada: VCH, Suite 909, 220 East 23rd Street, New York, NY 10010-4606 (USA)


ISBN 3-906390-14-4

此为试读, 需要完整PDF请访问: www.ertongbook.com

TO BARBARA

Jack D. Dunitz

X-Ray Analysis and the Structure of Organic Molecules



(2nd Corrected Reprint)



Verlag Helvetica Chimica Acta, Basel



Weinheim · New York · Basel
Cambridge · Tokyo

Prof. Dr. Jack D. Dunitz
Laboratorium für Organische Chemie
ETH-Zentrum
Universitätstrasse 16
CH-8092 Zürich

This book was carefully produced. Nevertheless, editor and publisher do not warrant the information contained therein to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details, or other items may inadvertently be inaccurate.

Published jointly by
VHCA, Verlag Helvetica Chimica Acta, Basel (Switzerland)
VCH Verlagsgesellschaft mbH, Weinheim (Federal Republic of Germany)
VCH Publishers, Inc., New York, NY (USA)

Editorial Director: Dr. M. Volkan Kisakürek
Production Manager: Jakob Schüpfer
Cover Design: Bruckmann & Partner, Basel

Library of Congress Card No. applied for.

A CIP catalogue record for this book is available from the British Library.

Die Deutsche Bibliothek – CIP-Einheitsaufnahme
Dunitz, Jack D.:
X-ray analysis and the structure of organic molecules / by Jack
D. Dunitz. – 2., corr. reprint. – Basel : VHCA ; Weinheim ;
New York : VCH, 1995
ISBN 3-906390-14-4

© Verlag Helvetica Chimica Acta, CH-4010 Basel, Switzerland, 1995

Printed on acid-free paper.

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Printing: Birkhäuser+GBC AG, CH-4153 Reinach BL
Printed in Switzerland

Preface

This book has developed out of a series of lectures given at Cornell University in September and October 1976 when I held the George Fisher Baker Non-Resident Lectureship in Chemistry. I am most grateful to the Baker Lecture Committee for the invitation to act as Baker Lecturer. Thanks to the friendship and hospitality of my hosts, who did everything possible to make me feel at home at Cornell, the weeks I spent there were a rich and happy experience that I shall cherish to the end of my days.

The task of producing a finished manuscript has been greatly eased by the help I have had from several friends and colleagues. Parts of the original manuscript were read by Kevin Brown, Hans-Beat Bürgi, Erik Bye, Derek Chadwick, Phillip Coppens, Volker Gramlich, Christoph Kratky, Richard Rosenfield, Bernd Schweizer, Paul Seiler, and Fritz Winkler; I am grateful to them all for their constructive comments and criticisms. I owe special thanks to Kenneth Trueblood of the University of California at Los Angeles for reading virtually the entire first version of the manuscript, for drawing my attention to countless errors, ambiguities, and stylistic inelegancies in it, and for suggesting numerous ways of improving the quality and intelligibility of the text. It was most fortunate for me that Ken chose to spend a sabbatical year in my laboratory in Zurich, where I could benefit from almost daily discussions with him. I am also indebted to Max Dobler for providing me with X-ray photographs and diagrams for several figures and for preparing the computer programs that are listed in the two appendices.

Chapter 10 contains previously unpublished material that was developed in the course of a long-standing collaboration with Hans-Beat Bürgi, and I am very grateful to him for his generous permission to include this material here under my own name.

I must also acknowledge my indebtedness to the many other researchers who have contributed, knowingly or unknowingly, to the subject matter of this book. Where possible, I have indicated my sources of information by literature references. These are fairly complete as far as factual knowledge is concerned, but they are hopelessly inadequate in

Preface

assigning credit for ideas. More often than not, the origins of ideas are forgotten, if they are ever consciously known. Like many scientists, I have the habit of absorbing fragments of other people's ideas—from lectures, from books, from conversations—and nurturing them as my own. In my opinion, science lives on this kind of cross-fertilization, so I hope I need not feel too guilty about such borrowings.

Many readers will not have to be told that the quotations at the beginning of each chapter are from Lewis Carroll, but for readers who were not brought up among English books I had better explain that Lewis Carroll was the pseudonym of a nineteenth-century mathematician, Charles Lutwidge Dodgson (1832–1898), one of the founders of mathematical logic and the author of *Alice's Adventures in Wonderland* and *Through the Looking Glass*.

Finally, I must record my appreciation to my secretary, Lucie a Marca, for her skill in typing the manuscript and for her patience in coping with its innumerable modifications, emendations, and revisions.

Zurich

JACK DUNITZ

Preface to Corrected Reprint, 1995

The first edition of this book contained errors and misprints. I am obliged to many friends and colleagues for their careful reading of the text and for informing me about the errors they detected. Most are harmless, but some might be sources of confusion. Now that the first edition is out of print, Dr. M. Volkan Kısakürek has kindly offered to produce a corrected reprint under the auspices of *Helvetica Chimica Acta Publishers*, and I am most grateful to him for this initiative.

Zurich, June 1995

JACK DUNITZ

Contents

Introduction	17
PART ONE: CRYSTAL STRUCTURE ANALYSIS	
1. Diffraction of X-Rays by Crystals	25
Scattering	25
Superposition of waves	25
Interference	27
Fourier transforms	29
Scattering by a point atom	31
Scattering by an assemblage of point atoms	32
Scattering by a periodic array: diffraction	33
Further properties of Fourier transforms: convolution	38
Scattering by atoms	42
Effect of atomic vibrations	43
Transform of a molecule	49
Disorder	52
The crystal as a Fourier series	59
The Patterson function	63
2. Internal Symmetry of Crystals	73
Historical background	73
Space lattices	74
Space groups	82
Space group $P\bar{1}(C_i)$	85
Space group $P2_1/c(C_{2h}^5)$	90
Space group $P2_12_12_1(D_2^4)$	93
Determination of space group	96
Intensity statistics	99
Space groups and molecular symmetry	103
Molecular packing arrangements	106
3. Methods of Crystal Structure Analysis	112
Statement of the problem	112
Trial-and-error analysis	113

Contents

Heavy-atom methods	117
Method of isomorphous replacement	123
Anomalous scattering: determination of absolute configuration	129
Direct methods	148
A simple example	149
Unitary and normalized structure factors	153
Equalities and inequalities	156
Sayre's equation	161
Probability relationships	162
Practical application of direct methods	165
Structure invariants and semi-invariants: origin and enantiomorph specification	172
Aberrant structure invariants	178
Summary of direct-method procedures	181
4. Methods of Crystal Structure Refinement	183
Structure refinement: the R factor	183
The difference synthesis	185
Least-squares analysis	191
Least-squares analysis in crystal structure refinement	200
Intrinsic parameter correlation	207
Constrained refinement	209
Least-squares weights	213
Wrong structures	222
5. Treatment of the Results	225
Long lists of numbers	225
Hazards of oblique coordinate systems	226
Linear transformations	232
Transformation from triclinic to orthonormal axes	235
Calculations in Cartesian coordinates	240
Thermal motion analysis	244
The Cruickshank model	245
Effect of libration on apparent intramolecular distances	248
General treatment of rigid-body vibrations	249
Nonrigid-body thermal motion analysis	257
Lattice-dynamical treatment of rigid-body motion	260
Accuracy of derived parameters	261
6. Experimental Aspects of X-Ray Analysis	266
Introductory remarks	266
Photographic methods	267
Rotation and oscillation photographs	268

Weissenberg photographs	270
Precession photographs	273
Single-crystal diffractometers	276
The integrated intensity	281
Polarization factor	283
Lorentz factor	284
Absorption	287
Extinction	290
Double reflection	296

PART TWO: MOLECULAR STRUCTURE

7. Crystal Structure Analysis and Chemistry	301
Growth of information on molecular structures	301
Molecular structural formulas	305
Conformational analysis	312
Solid-state organic chemistry	319
Reaction intermediates	323
Molecular potential energy surfaces	325
<i>Cis-trans</i> isomerization of amides	328
From crystal structure data to chemical reaction paths	337
Linear triatomic species	341
Bond number relationship	347
Ligand exchange at tetrahedral cadmium	348
Tetrahedral molecules and ions	354
Structural correlation principle	363
Nucleophilic addition to carbonyl groups	366
Other structural correlations	384
8. Electron-Density Distributions in Molecules	391
Electron-density difference maps	391
Neutron diffraction	393
An example: <i>p</i> -nitropyridine- <i>N</i> -oxide	395
Residual density features in organic molecules	400
Difference densities by least-squares analysis	406
Comparison with theoretical deformation densities	409
Net charges on atoms	412
Summary and outlook	415
9. Geometric Constraints in Cyclic Molecules	418
Geometric constraints	418
Four-membered rings	423
Five-membered rings	425

Contents

Six-membered rings	431
Six-membered rings and octahedra	436
Other approaches to the flexibility problem	438
Larger rings	439
Bicyclic systems	440
Polycyclic molecules with high symmetry	444
10. Conformational Maps and Space Groups	447
One-dimensional torsional potential functions and line groups	447
Two torsional degrees of freedom	450
An example: diphenylmethane	450
Other examples: the frame symmetry group	460
Ligand permutations	463
Three torsional degrees of freedom	466
Triphenylmethane	466
Dibenzyl	475
Trimethylboron	478
Four-dimensional space groups	481
1,1,1-Trichloropentane	483
Tetraphenylmethane and related molecules	484
APPENDICES	
I. A BASIC computer program for calculating interatomic distances and angles and torsion angles from crystal coordinates	495
II. A BASIC computer program for calculating Cartesian coordinates from internal coordinates	498
Index of Names	503
Index of Subjects	510

X-RAY ANALYSIS AND THE STRUCTURE OF ORGANIC MOLECULES

