

# **THE OPTICAL PROPERTIES OF ORGANIC COMPOUNDS**

**Alexander N. Winchell**

# THE OPTICAL PROPERTIES OF ORGANIC COMPOUNDS

Alexander N. Winchell  
*Emeritus Professor of Mineralogy*  
*The University of Wisconsin*

SECOND EDITION, ENLARGED AND COMPLETELY REVISED

ACADEMIC PRESS INC., PUBLISHERS  
New York, N. Y.

## Preface

In the first edition of this volume about sixteen hundred organic substances were described and about one thousand were placed on the diagram for the determination of compounds. In the brief time since that volume was published about seven hundred organic compounds have been described, as to optical properties, in scientific publications, and the American Cyanamid Company has generously released for publication in this volume data on the optical properties of about two hundred other organic compounds. Therefore, in this edition more than twenty five hundred substances are described and nearly two thousand are placed on one or both of the two diagrams for the determination of compounds.

In preparing the second edition of this volume the aim has been to include all organic compounds whose optical properties were described prior to October first, 1952, but there are undoubtedly some omissions, since such data are almost never indexed.

It is a pleasure to acknowledge the helpful cooperation of many persons in this work. The second Plate was prepared at the suggestion of Professor Horace Winchell of Yale University. Useful suggestions and data on optical properties of certain organic compounds have been supplied very generously by many colleagues, including W. L. Bond, Glenn Coven, R. L. Gilbert, F. T. Jones, C. L. Johnson, G. L. Keenan, Alan F. Kirkpatrick, W. J. McCrone, Charles Maresh, John Mitchell, E. M. Plein, C. F. Poe, T. G. Rochow, R. W. Stafford, and E. F. Williams.

Some organic compounds have structures which are not yet fully determined or are entirely unknown. Such substances are described after the others in a separate group ("Unclassified") in two parts (with and without nitrogen) each one arranged alphabetically according to the parent compound.

The classification of the many compounds added in the second edition was accomplished largely by the aid of Dr. Elga R. Wasserman.

It seems reasonable to include a brief description of carbon, as found in nature, as a sort of introduction to the description of organic compounds.

**Alexander N. Winchell**

88 Vineyard Road  
Hamden 17, Conn.

## Introduction

The aim has been to include all organic compounds whose optical properties are sufficiently well known to permit identification by optical methods. In general it has been found that correct identification requires (as a minimum) an accurate knowledge of the indices of refraction. Therefore this volume includes, so far as they are known, all organic compounds whose indices of refraction have been measured.

The compounds are arranged according to the method by which organic compounds are classified in the fourth edition of Beilstein's *Handbuch der organischen Chemie*, published by the German Chemical Society (deutsche chemische Gesellschaft). The Beilstein system is founded on the premise that every definite compound can be expressed in a structural formula. The system contains the following four main divisions:

Division I: Acyclic stem nuclei. The carbon atoms are joined in open chains only. (Volumes I-IV of Beilstein's *Handbuch*.)

Division II: Isocyclic stem nuclei. The carbon atoms are joined in closed rings which do not include other kinds of atoms as ring components. (Volumes V-XVI of Beilstein's *Handbuch*.)

Division III: Heterocyclic stem nuclei. The carbon atoms are joined in closed rings which include one or more other kinds of atoms as ring components. (Volumes XVII-XXVII of Beilstein's *Handbuch*.)

Division IV: Natural products not assigned places in the three preceding divisions. (Vols. XXX *et seq.* of Beilstein's *Handbuch*.)

The first three divisions are based on the structural formulas; the fourth includes natural products of indefinite composition or incompletely known structure.

Each of the four main divisions is further subdivided. Division I (acyclic) and Division II (isocyclic) each include some thirty-odd classes. For the most part corresponding classes are numbered the same in each division. Division III (heterocyclic) is classified first into subdivisions according to the kind and number of heterocyclic atoms; each of these subdivisions is then divided into classes in the same manner as Divisions I and II above. Division IV is arbitrarily divided into nine subdivisions.

Class I of Division I, Class I of Division II, and Class I of each subdivision of Division III may all be defined as stem nuclei and each subdivided according to the decreasing saturation of the several series of hydrocarbons which it includes, thus:

## Division I. Acyclic Compounds

## Class I. Compounds with no functional group

Subclass A. Saturated  $C_nH_{2n+2}$ Subclass B. Unsaturated  $C_nH_{2n}$ Subclass C. Unsaturated  $C_nH_{2n-2}$ , etc.

## Division II. Isocyclic Compounds

## Class I. Compounds with no functional group

Subclass A. Saturated  $C_nH_{2n}$ Subclass B. Unsaturated  $C_nH_{2n-2}$ Subclass C. Unsaturated  $C_nH_{2n-4}$  etc.

## Division III. Heterocyclic Compounds

## Subdivision I. Compounds with one oxygen atom in the cycle

## Class I. Compounds with no functional group

Subclass A. Saturated  $C_nH_{2n}O$ Subclass B. Unsaturated  $C_nH_{2n-2}O$ Subclass C. Unsaturated  $C_nH_{2n-4}O$ , etc.

The classes containing one or more functional groups in the molecule need to be further subdivided. For Class 2 (hydroxy compounds), which contains the hydroxy group, the subclasses in each division (except IV) are determined by the number of such groups in the molecule, thus:

## Division I. Acyclic Compounds

## Class 2. Hydroxy compounds

Subclass A. Monohydroxy compounds

Subclass B. Dihydroxy compounds

Subclass C. Trihydroxy compounds, etc.

## Division II. Isocyclic Compounds

## Class 2. Hydroxy compounds

Subclass A. Monohydroxy compounds, etc.

## Division III. Heterocyclic Compounds

## Subdivision 1. Compounds with one oxygen atom in the cycle

## Class 2. Hydroxy compounds

Subclass A. Monohydroxy compounds, etc.

The same method of subdivision is employed for the further division of the subclasses as for Class 1 -- that is, according to the decreasing saturation of its component series, thus:

## Division I. Acyclic Compounds

## Class 2. Hydroxy compounds

Subclass A. Monohydroxy compounds

Section 1. Monohydroxy compounds  $C_nH_{2n+2}O$ Section 2. Monohydroxy compounds  $C_nH_{2n}O$ Section 3. Monohydroxy compounds  $C_nH_{2n-2}O$ , etc.

Each subclass is further arranged in a homologous series of groups of isomers in the order of increasing numbers of carbon atoms.

Carbonyl compounds (class 3 in Divisions I, II, and III) include aldehydes, ketones, ketenes, quinones, etc.

The numbers and letters used for classes and subclasses, respectively, are those given in Beilstein's *Handbuch*. It will be observed that many of the classes and subclasses found in Beilstein are not included here, the reason being that no representatives of these classes have been measured optically.

For a complete description of the classification system the reader is referred to the introduction of volume I of the principal work and to Huntress' excellent monograph<sup>1</sup>.

Every principal volume of the fourth edition covers the chemical literature up to January 1, 1910. The First Series of supplementary volumes covers the literature published between 1910 and 1919. As the present work was being prepared, the principal and supplementary volumes covering Divisions I, II, and III (Volumes I-XXVII inclusive) and Volumes XXX (rubber and carotenoids) and XXXI (carbohydrates I) were available. For Division IV (Volumes XXX *et seq.*) the principal and first supplementary volumes are combined. Volumes XXVIII and XXIX are devoted to an alphabetical index to the preceding volumes. The numerous compounds not included in the volumes of Beilstein thus far published have been placed where they will presumably appear in future supplementary volumes.

In one detail the classification used in this book differs from that of Beilstein. He arranges the salts of each acid in the following order:  $\text{NH}_4$ ,  $\text{NH}_4\text{OH}$ ,  $\text{NH}_3$ ,  $\text{NH}_4^+$ , Li, Na, K, Rb, Cs, Cu, Ag, Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, Hg, B, Al, Ga, In, Tl, Sc, Y, La, Ce, Pr, Nd, Ta, As, Sb, Bi, Cr, Mo, W, U, Mn, Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt. Acid salts precede neutral salts, which are followed by basic salts. Salts containing two or more metals are always listed with the salts of the metal which comes last in the series. All hydrated salts are included with the corresponding anhydrous salts. This arrangement however, does not always bring together those salts which are isomorphous and are therefore so closely related that in some cases they can intercrystallize in any proportions to form homogeneous crystals. Since such intercrystallizations are common in nature and can be recognized by their optical properties, it seems highly advantageous to modify the classification so as to bring them together. To do this it is necessary to deal with anhydrous and hydrated salts separately and to modify somewhat the order of the metals. Accordingly the anhydrous salts of all the metals are listed first, and these are followed by the monohydrates of all the metals, the dihydrates, the trihydrates, etc. Moreover, the order in which the anhydrous salts, for example, are listed must sometimes be modified to bring the isomorphous salts together. Thus ammonium salts are never isomorphous with lithium salts so far as known, but are frequently isomorphous with potassium salts, and in some cases both of these are miscible with sodium salts, as illustrated in certain tartrates like Seignette salts.

---

<sup>1</sup>Huntress, *A Brief Introduction to the Use of Beilstein's Handbuch der organischen Chemie*, 2d ed., John Wiley, 1938.

It seems reasonable to include a brief description of carbon, as found in nature, as a sort of introduction to the description of organic compounds.

Since the nomenclature of organic chemistry is still unsettled, the choice of names for given compounds in this volume is necessarily somewhat arbitrary. Wherever possible, the name adopted by the International Commission on the Reform of the Nomenclature of Organic Chemistry<sup>1</sup> is given first; this is followed by such other names as seem to have attained wide usage. Compounds such as the sugars and their derivatives, as well as double salts and some naturally occurring compounds which are not readily named according to the systematic scheme, are listed only by their common names.

In abbreviating citations to the original literature, the usage of *Chemical Abstracts* has been followed.

According to George L. Keenan<sup>2</sup> indices of 3,5-dinitrobenzoyl derivatives of various organic compounds may be determined most readily and satisfactorily by the immersion method (see J. Assoc. Official Agr. Chem. 13, 389, 1930) in solutions of potassium mercuric iodide in glycerol and water, although for rapid determinative work oily liquids consisting of mixtures of mineral oils, monochloronaphthalene and methylene iodide can be used.

W. M. D. Bryant<sup>3</sup> used liquids as follows:

$N_D = 1.36-1.40$ , glycerol-glycol-water.

$N_D = 1.40-1.72$ , potassium mercuric iodide-glycerol-water.

$N_D = 1.74-1.78$ , methylene iodide-sulfur.

$N_D = 1.85-2.10$ , methylene iodide-arsenic trisulfide.

In 1910 Bolland<sup>4</sup> published optic data for about 450 substances which had not previously been measured; of these more than half (275) were organic compounds. This is a far greater number of new measures than have been reported by any other writer at any time, but the value of Bolland's work is seriously impaired by its imperfections. Thus he usually studied the crystallized substance only in the position in which it happened to lie, which was often on the largest face (or cleavage surface). Accordingly he described the extinction as "parallel" if it was parallel with the edges of that face. Moreover, he called the extinction parallel if it were approximately so,  $20^\circ$  being the smallest angle he recognized as a deviation from the parallel. Any monoclinic crystal which is platy or tabular on any face parallel to  $b$  has "parallel extinction" in Bolland's usage, and a monoclinic or triclinic crystal having an extinction angle of less than  $20^\circ$  in its platy crystals is described in the same way.

Bolland determined the sign of elongation from a single plate, so that it is always reported as plus or as minus, never as  $\pm$ .

For only a few substances does Bolland give three indices of refraction; nearly always he gives only the two indices that can be measured in the position of the plates. He does not give these as  $N_x$  and  $N_z$ , but later writers, including

<sup>1</sup>Patterson, J. Am. Chem. Soc., 55, 3905 (1933).

<sup>2</sup>J. Am. Chem. Soc. 63, 1924 (1931).

<sup>3</sup>J. Am. Chem. Soc. 64, 3758 (1932).

<sup>4</sup>Sitzber. Akad. Wiss. Wien. 119, Abt. II, b, 275 (1910); Monatsh. 31, 387 (1910).

Landolt-Bornstein and the compilers of the International Critical Tables, quote Bolland's figures as referring to biaxial crystals and as being  $N_X$  and  $N_Z$ . Actually they might be (1) the two indices of a uniaxial crystal, (2) any two of the three chief indices of a biaxial crystal, or even (3) any two values intermediate between  $N_X$  and  $N_Z$ . They are the indices for the fast ray and the slow ray normal to the plate studied, whatever its orientation may be. Some other workers have used the same system, notably Kley, Mayrhofer, and Gatewood. In this book such measures are given as values of  $N_1$  and  $N_2$  to distinguish them from true values of the principal indices.

Bolland's data for refractive indices, since they are not very accurate, are not always included in this book when other data are at hand. But for many substances no other measures have been published. To give a clear idea of the range of accuracy in Bolland's data, Table I has been prepared, which shows how his values compare with more accurate measures in certain cases which are believed to be representative.

Kofler<sup>1</sup> has shown that some of the early measures of indices of refraction seem to be incorrect not because of errors in those measures but because they were made on material not accurately described; for example, anhydrous substances were not distinguished from hydrous in the case of caffeine, codeine, morphine, and orthoform; or different crystal phases of a single substance were not distinguished, as in the case of veronal and morphine. Table II illustrates these points.

The first edition of this volume was the result of several years' work supported by grants from the Wisconsin Alumni Research Foundation. It is a pleasure to acknowledge the aid of many persons in the work. Data on optical properties of certain compounds were kindly supplied by W. M. D. Bryant, R. C. Emmons, H. W. Hartline (unpublished thesis received from N. W. Buerger), G. L. Keenan, C. W. Mason, C. F. Poe, C. D. West, R. E. Wilcox, and Mary L. Willard. Optical measures of some compounds were made at the University of Wisconsin by R. G. Comer, R. C. Emmons, and J. J. Marais. The classification of the compounds was accomplished chiefly with the aid of Drs. E. Leon Foreman, Minnie Meyers, and Ivan Wolff, and the final editing was done by Dr. Leonard T. Capell, associate editor of *Chemical Abstracts*.

---

<sup>1</sup>Mikro. Meth. Mikroch., 1936, pp. 91 and 92.



Table I. *Comparison of Data.*

Substance	Crystal System	Chief form	Extinction		Recent Data*		Bolland		Recent Data*	Bolland		Recent Data*
			Bolland	In 010	Nx	N <sub>1</sub>	N <sub>x</sub>	N <sub>y</sub>		N <sub>z</sub>	N <sub>s</sub>	
Li <sub>2</sub> SO <sub>4</sub> · H <sub>2</sub> O	Mono.	{101}	Parallel	—36°	1.459	1.48			1.477			1.488
Na <sub>2</sub> SO <sub>3</sub>	Hex.				1.515	1.54						1.565
Na <sub>3</sub> PO <sub>4</sub> · 12 H <sub>2</sub> O	Trig.				1.458	1.44						1.4524
KCNS	Mono.	{110}	Parallel	16°	1.532		1.605	1.645	1.660	1.73		1.730
KClO <sub>3</sub>	Mono.	{001}			1.410	1.47			1.517			1.524
H <sub>2</sub> KPO <sub>4</sub>	Tet.	{100}	Parallel	0°	1.4684	1.47			1.482		1.54	1.5095
HKCO <sub>3</sub>	Mono.	{101}	Parallel	+30°	1.380	1.48			1.7380	1.95+	1.57	1.578
K <sub>4</sub> Cr <sub>2</sub> O <sub>7</sub>	Tri.	{010}	Parallel		1.7202		1.75	1.95	1.7245 D			1.8197
K <sub>2</sub> CrO <sub>4</sub>	Orth.	Varied	Parallel		1.6873				1.7261			1.7305 C
					1.7087	1.72			1.7261		1.74	1.7304
HKC <sub>2</sub> O <sub>4</sub>	Mono.	{001}, {010}	Inclined		1.415		1.46	1.54	1.545	1.55		1.565
HRbC <sub>4</sub> H <sub>4</sub> O <sub>6</sub>	Orth.	{010}, {001}	Parallel		1.5101	1.52			1.5495		1.58	1.5833
CuSO <sub>4</sub> · 5 H <sub>2</sub> O	Tri.	{111}	Parallel	Incl.	1.5141	1.53			1.5368		1.54	1.5434
AgNO <sub>3</sub>	Orth.	{001}			1.729	1.73			1.744		>1.75	1.788
Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>4</sub>	Mono?				1.485	1.485			1.488		1.49	1.489
H <sub>2</sub> Ca(C <sub>4</sub> H <sub>4</sub> O <sub>6</sub> ) <sub>2</sub> · 6 H <sub>2</sub> O	Orth.	{110}, {010}	Parallel		1.495	1.51			1.507		1.545	1.545
BaCl <sub>2</sub> O <sub>6</sub> · H <sub>2</sub> O	Mono.	{001}, {110}	Parallel		1.562	1.58			1.577		1.63	1.635
HgCl <sub>2</sub>	Orth.	{011}, {001}	Parallel		1.725		1.63	1.74	1.859	1.95		1.965
Hg(CN) <sub>2</sub>	Tet.	{110}	Parallel		1.492	1.60					1.65	1.645 ±

\* Believed to be accurate.

Table II. *Refractive Indices*

Substance	Bolland <sup>1</sup> , 1910	Behrens- Kley	Mayrhofer	Kofler
Caffeine		1.54 1.66		Anhydrous: 1.446; 1.70 <i>ca.</i> Hydrous: 1.421; 1.661 <i>ca.</i> ; 1.689 <i>ca.</i>
Codeine		1.56 1.66		Anhydrous: 1.616 <i>ca.</i> ; 1.622 <i>ca.</i> ; 1.645 <i>ca.</i> Hydrous: 1.542 > 1.660
Morphine		1.62 1.63		Anhydrous, Phase I: 1.653; 1.657; 1.671 Anhydrous, Phase II: 1.573; 1.625; 1.630 Hydrous: 1.582; 1.623; 1.644
Orthoform			1.515 1.523 (1.528; 1.587)	Anhydrous: 1.622; 1.658 Hydrous: 1.515; 1.523
Veronal			1.436; 1.552; 1.577	Phase I (Stable): 1.526; 1.570 Phase II (Unstable): 1.473; 1.558; 1.580 Phase III (Unstable): 1.473 <i>ca.</i> ; 1.573 <i>ca.</i>
Narcotine	1.54 1.69	1.54 1.69		1.525; 1.687 <i>ca.</i> ; 1.697 <i>ca.</i>
Arabinose	1.545 1.56			$\alpha$ -D 1.551; 1.567; 1.571 $\beta$ -D 1.555; 1.573; 1.577; E. T. Wherry: J.A.C.S., XL, 1852
Fructose or Levulose	1.55 1.56			1.558; ?; 1.561 G.L. Keenan: J.W.A.S., XVI, 433
Urea	1.485 1.61		1.485 1.600	1.484; 1.602 E. T. Wherry: J.W.A.S., VIII, 277
Phenacetin	1.54; 1.58; 1.59		1.523; 1.532; 1.587	
Santonin	1.61 1.62		1.589; 1.592; 1.639	1.590; 1.630; 1.640 — Int. Crit. Tables, I, 256, 280

<sup>1</sup> Sitzb. Akad. Wiss. Wien, 119, II, b, 275 (1910); 117, II, b, 671 (1908).

## LIST OF ABBREVIATIONS AND SYMBOLS

(Names of periodicals and symbols of chemical elements not included.)

A, B = optic axes of biaxial crystals.

A, B, C, D, E, F, G, H (after indices of refraction) = various types of monochromatic light.

Å = Ångstrom (one hundred-millionth of a centimeter).

*a* = front and rear crystal axis.

$\alpha$  = angle between crystal axes *b* and *c* in the positive octant.

[ $\alpha$ ] = specific rotation, or the angle through which the plane of polarization is turned by a liquid or solution containing one gram of substance in one cc. of liquid in a layer one decimeter deep.

B = birefringence.

*b* = right and left crystal axis.

B.P. = boiling point.

$\beta$  = angle between crystal axes *a* and *c* in the positive octant.

C, see A, B, etc., above.

*c* = concentration.

*c* = vertical crystal axis.

*ca.* = about.

calc. = calculated.

$\gamma$  = angle between crystal axes *a* and *b* in the positive octant.

D = density.

E = extraordinary ray.

E, see A, B, etc., above.

2E = apparent optic angle measured in air.

F, see A, B, etc., above.

G, see A, B, etc., above.

H = hardness. See also A, B, etc., above.

2H = the apparent optic axial angle measured in oil.

Li (after index of refraction) = lithium (red) light.

$\lambda$  = a wave length of monochromatic light.

M.P. = melting point or fusion temperature.

N = index of refraction.

Na (after index of refraction) = sodium (yellow) light.

$N_E$  = index of refraction for the extraordinary ray.

$N_i$  = an intermediate index of refraction.

$N_O$  = index of refraction for the ordinary ray.

$N_X$  = index of refraction for the ray vibrating along X = *a* of some writers.

$N_{X'}$  = index of refraction for the fast ray in a certain position.

$N_Y$  = index of refraction for the ray vibrating along Y = *b* of some writers.

$N_Z$  = index of refraction for the ray vibrating along Z = *c* of some writers.

- $N_{2'}$  = index of refraction for the slow ray in a certain position.  
 $N_1$  = one index of refraction; it may have any value from  $N_X$  to  $N_Y$ .  
 $N_2$  = a second index of refraction; it may have any value from  $N_Y$  to  $N_Z$  unless  $N_3$  is also given, when it is merely an intermediate value.  
 $N_3$  = a third index of refraction (the highest one measured).  
 $n$  = an indefinite number.  
 $0 > E$  or  $0 < E$  = absorption greater (or less) for the 0 ray than for the E.  
 $r > v$  or  $r < v$  (after the optic angle) signifies that the optic angle in red light is greater than or less than the optic angle in violet light.  
 Ref = Reference. See the List of References, pages 319-336.  
 Tl (after index of refraction) = thallium (green) light.  
 U.C. = unit cell.  
 $2V$  = the true angle between the optic axes.  
 $X$  = the vibration direction of the fastest ray. =  $a$  of German writers.  
 $Y$  = the vibration direction of the intermediate ray. =  $b$  of German writers.  
 $Z$  = the vibration direction of the slowest ray. =  $c$  of German writers.  
 $X > Y$ , etc. = absorption greater for light vibrating along  $X$  than for light vibrating along  $Y$ , etc.  
 $^\circ$  = degree of temperature (Centigrade) or an angle whose unit is measured by one 360th of a circle.  
 $\wedge$  = angle; for example,  $Z \wedge c$  = the angle between  $Z$  and  $c$ .  
 $>$  = greater than.  
 $<$  = less than.  
 $\perp$  = normal to.  
 $\parallel$  = parallel; this is often omitted, as in the statement: the optic plane is 010; or it is replaced by =, as in  $X = a$ .  
 $\therefore$  = therefore.  
 100, 010, 001, 110, 101, etc. = Miller symbols of crystal directions.  
 {100}, {010}, {001}, {110}, etc. = Miller symbols of crystal forms.

The optic sign of a substance is expressed by (+) or (—) before the expression for the optic angle; for example, (+)  $2V = 50^\circ$  signifies that the true acute angle between the optic axes is  $50^\circ$  and that this is measured about  $Z$  so that the optic sign is positive.

The sign of elongation of crystals is positive if  $Z$  (the vibration direction of the slow ray) is parallel with, or less than  $45^\circ$  from, the direction of elongation; it is negative if  $X$  (the vibration direction of the fast ray) occupies this position; it is plus or minus ( $\pm$ ) if  $Y$  occupies the position named.

In monoclinic crystals the extinction angle is commonly measured from the vertical axis to  $Z$ , if that is possible; if not, the measure may be to  $X$ . This angle is sometimes considered positive (+) if it is measured in the obtuse angle  $\beta$  between the axes  $a$  and  $c$ ; and negative (—) if it is in the acute angle  $\beta$ . It seems better to consider this angle as positive (+) if it is measured (when the observer is looking from a position in the positive octant bounded by +  $a$ , +  $b$ , and +  $c$  toward the negative octant) by turning the crystal on the stage clockwise from an extinction position to a crystal direction (usually  $c$ , the long direction of the crystal).

## Table of Contents

PREFACE . . . . .	iii
INTRODUCTION . . . . .	ix

### Descriptions of Substances

#### PRELIMINARY

Carbon . . . . .	1
Coal . . . . .	1

#### I. Acyclic Compounds

Class 1. Compounds Containing No Functional Group . . . . .	3
Class 2. Hydroxy Compounds . . . . .	5
Class 3. Carbonyl Compounds . . . . .	11
Class 4. Carboxylic Acids . . . . .	13
Subclass A. Monocarboxylic Acids and Derivatives . . . . .	13
Subclass B. Dicarboxylic Acids and Derivatives . . . . .	26
Subclass C. Tricarboxylic Acids and Derivatives . . . . .	36
Subclass D. Tetracarboxylic Acids and Derivatives . . . . .	37
Subclass L. Hydroxy Carboxylic Acids and Derivatives . . . . .	37
Subclass M. Carbonyl Carboxylic Acids and Derivatives . . . . .	59
Class 6. Sulfonic Acids and Derivatives . . . . .	59
Subclass E. Keto Sulfonic Acids and Derivatives . . . . .	59
Class 8. Amines and Derivatives . . . . .	61
Class 10. Hydrazines . . . . .	72
Class 19. Carbon-Phosphorus Compounds . . . . .	72
Class 20. Carbon-Arsenic Compounds . . . . .	72
Class 32. Carbon Thallium Compounds . . . . .	73

#### II. Isocyclic Compounds

Class 1. Compounds Containing No Functional Group . . . . .	73
Class 2. Hydroxy Compounds . . . . .	84
Class 3. Carbonyl Compounds . . . . .	103
Class 4. Carboxylic Acids . . . . .	111
Subclass A. Monocarboxylic Acids . . . . .	111
Subclass B. Dicarboxylic Acids and Derivatives . . . . .	122
Subclass C. Tricarboxylic Acids and Derivatives . . . . .	126
Subclass F. Hexacarboxylic Acids and Derivatives . . . . .	126
Subclass J. Hydroxycarboxylic Acids and Derivatives . . . . .	126
Subclass K. Carbonyl Carboxylic Acids . . . . .	133
Subclass L. Hydroxy Carbonyl Carboxylic Acids and Derivatives . . . . .	133

Class 6. Sulfonic Acids and Derivatives . . . . .	133
Class 9. Amines and Derivatives . . . . .	139
Subclass A. Monoamines and Derivatives . . . . .	139
Subclass B. Diamines and Derivatives . . . . .	153
Subclass G. Hydroxyamines and Derivatives . . . . .	154
Subclass H. Carbonyl Amines and Derivatives . . . . .	160
Subclass J. Hydroxy Carbonyl Amines and Derivatives . . . . .	161
Subclass K. Amino Carboxylic Acids and Derivatives . . . . .	162
Subclass L. Amino Hydroxy Carboxylic Acids and Derivatives . . . . .	164
Subclass P. Amino Sulfonic Acids and Derivatives . . . . .	166
Subclass Q. Amino Hydroxy Sulfonic Acids and Derivatives . . . . .	170
Subclass R. Amino Carbonyl Sulfonic Acids and Derivatives . . . . .	171
Class 10. Hydroxylamines and Derivatives . . . . .	171
Class 11. Hydrazines and Derivatives . . . . .	171
Class 12. Azo Compounds . . . . .	175
Class 14. Azoxy Compounds . . . . .	179
Class 25. Carbon-Arsenic Compounds . . . . .	180
Class 27. Carbon-Bismuth Compounds . . . . .	180
Class 28. Carbon-Antimony Compounds . . . . .	181
Class 35. Carbon-Mercury Compounds . . . . .	181

### III. Heterocyclic Compounds

1. Compounds with One Oxygen Atom in the Cycle . . . . .	181
Class 1. Compounds with No Functional Group . . . . .	181
Class 2. Hydroxy Compounds . . . . .	182
Class 3. Carbonyl Compounds . . . . .	182
Class 4. Carboxylic Acids and Derivatives . . . . .	187
2. Compounds with Two Oxygen Atoms in the Cycle . . . . .	191
Class 1. Compounds with No Functional Group . . . . .	191
Class 2. Hydroxy Compounds . . . . .	191
Class 3. Carbonyl Compounds . . . . .	191
6. Compounds with Six Oxygen Atoms in the Cycle . . . . .	193
Class 1. Compounds with No Functional Group . . . . .	193
9. Compounds with One Nitrogen Atom in the Cycle . . . . .	193
Class 1. Compounds Containing No Functional Group . . . . .	193
Class 2. Hydroxy Compounds . . . . .	196
Class 3. Carbonyl Compounds . . . . .	197
Class 4. Carboxylic Acids and Derivatives . . . . .	200
Class 5. Sulfonic Acids and Derivatives . . . . .	201
Class 6. Amines and Derivatives . . . . .	201
10. Compounds with Two Nitrogen Atoms in the Cycle . . . . .	204
Class 1. Compounds Containing No Functional Group . . . . .	204
Class 2. Hydroxy Compounds . . . . .	206
Class 3. Carbonyl Compounds . . . . .	207
Class 4. Carboxylic Acids and Derivatives . . . . .	236
Class 5. Sulfonic Acids and Derivatives . . . . .	238
Class 7. Amines and Derivatives . . . . .	239
11. Compounds with Three Nitrogen Atoms in the Cycle . . . . .	243
Class 1. Compounds Containing No Functional Group . . . . .	243
Class 3. Carbonyl Compounds . . . . .	243
Class 7. Amines and Derivatives . . . . .	244

12. Compounds with Four Nitrogen Atoms in the Cycle . . . . .	246
13. Compounds with One Nitrogen and One Oxygen Atom in the Cycle . . . .	252
14. Compounds with Two Nitrogen Atoms and One Oxygen Atom in the Cycle	257

#### IV. Organic Compounds Not Assigned Places in the Three Preceding Groups

1. Carotenoids . . . . .	257
2. Carbohydrates . . . . .	257
3. Steroids or Derivatives of Perhydrocyclopentanophenanthrene . . . . .	274
5-Cholesten-3-ol or Cholesterol and its Derivatives . . . . .	274
4. Alkaloids . . . . .	277
Alkaloids of the Aromatic Amine Type . . . . .	277
Alkaloids with a Pyrrole Nucleus . . . . .	277
Pyridine Alkaloids . . . . .	278
Alkaloids with Condensed Pyrrolidin and Piperidine Rings . . . . .	279
Alkaloids of the Broom and Lupin Group . . . . .	283
Quinoline Alkaloids . . . . .	283
Isoquinoline Alkaloids . . . . .	293
Morphine and Cryptopine Alkaloids; Colchicine . . . . .	296
Carboline Alkaloids . . . . .	299
Alkaloids of Ergot, Pilocarpine, and Eserine . . . . .	299
Alkaloids of Unknown Constitution . . . . .	305
Strychnos Alkaloids . . . . .	306
5. Miscellaneous Compounds . . . . .	309
Nitrogenous substances . . . . .	309
Nitrogen-free substances . . . . .	310
REFERENCES . . . . .	319
REFERENCES ADDED FOR THE SECOND EDITION . . . . .	329
SUPPLEMENTARY DETERMINATIVE TABLES BASED ON REFRACTANCE . . . . .	337
INDEX . . . . .	395
EXPLANATION OF DIAGRAMS FOR THE DETERMINATION OF COMPOUNDS . . . .	441
KEY TO DIAGRAMS 1 AND 2 . . . . .	445

## I. ACYCLIC COMPOUNDS

### Carbon

*Carbon* (C) has at least two crystal phases<sup>1</sup>. One (the diamond) is isometric, commonly in octahedrons; also dodecahedral or cubic; perfect 111 cleavage.  $H = 10$ .  $D = 3.52$ . Infusible. Insoluble. Isotropic with  $N = 2.4135$  Li, 2.4195 Na, 2.4278 Tl. Colorless or tinted. Another phase is hexagonal (graphite) with  $c/a = 2.760$ .  $a = 2.46$ ,  $c = 6.80$  Å. U.C. 4. Crystals rounded hexagonal lamellae with perfect 0001 cleavage.  $H = 1 - 2$ .  $D = 2.25$ . Infusible. Insoluble. Opaque in thin section, but translucent in greenish-gray light in flakes made on a streak plate. Uniaxial negative with  $N$  between 1.93 and 2.07. Birefringence not strong. Color black; streak on smooth porcelain greenish black. When treated with  $HNO_3$  and  $KClO_3$  it changes to graphitic acid which has nearly the same optic properties, but is pleochroic with  $O =$  dark green and  $E =$  almost colorless. On heating it changes back to graphite.

### Coal

The carbon in coal is not diamond nor graphite, although in anthracite it is nearly pure. Recent work has shown that the refractive index of vitrain is a good indication of the quality of the coal. Thus, Fisher found that vitrain

Material	Source	Fixed Carbon	$N \perp$ Bedding	$N \parallel$ Bedding	Properties
Vitrain	Leicester	61.3	1.67	1.67	Free burning and coking coals
Vitrain	Warwick	63.1	1.70	1.70	
Vitrain	Lancaster	63.8	1.77	1.77	
Vitrain	S. Wales	74.5	1.87	1.81	Coking coals
Vitrain	Kent	80.8	1.84	1.84	
Vitrain	S. Wales	86.2	1.91	1.86	Steam coals
Vitrain	S. Wales	88.8	1.90	1.89	
Vitrain	S. Wales	93.6	1.90	1.80	Anthracites
Vitrain	Kilkenny	97.1	1.91	1.77	

<sup>1</sup> Graphite and diamond are minerals, but graphite (also diamond?) is derived from organic matter at least in some cases, and coal is clearly of organic origin.



of bituminous coal had  $N = 1.76$  and vitrain of semibituminous coal had  $N = 1.87$ . Also Cannon and George found the results tabulated on page 1 and shown in Fig. 1.

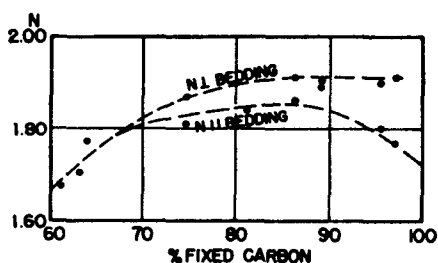


Fig. 1. Optic properties of vitrain.

*McCabe and Quirke furnish the following data:*

Material	Source	Fixed Carbon	Volatile Matter	Moisture	B.T.U.	N
1. Woody lignite	Hernando, Miss.	31.2	32.9	32.1	7048	1.632
2. Vitrain	Lafayette, Colo.	46.4	29.5	21.7	10265	1.703
3. Vitrain	Pershing, Iowa	45.6	34.4	18.7	11540	1.715
4. Vitrain	Middle Grove, Ill.	49.74	33.61	16.0	12188	1.723
5. Vitrain	Roanoke, Ill.	49.6	33.5	15.7	12303	1.723
6. Vitrain	Booneville, Ind.	49.50	40.60	9.18	13240	1.750
7. Vitrain	Harrisburg, Ill.	58.0	35.7	3.7	14160	1.768
8. Vitrain	Gibsonia, Ill.	55.9	40.1	2.3	14769	1.768
9. Vitrain	Hartshorne, Okla.	73.28	23.92	0.56	15680	1.795

Ref: 429a, 459, 465, 549, 556.