radii decrease in a regular way as the atomic number increases, while the configuration of the outer electrons is changed relatively little. Among the compounds which we have studied are the oxychlorides of composition MOCl, where M is a rare earth element. Of these, structures have been reported only for LaOCl,[1] PrOCl[2] and NdOCl[2] which have the PbFCl type[3] structure. Our work was stimulated by a correlation now being made by Koch and Cunningham of the thermodynamic properties of these substances[4,5] with crystal geometry.

Experimental

The oxychlorides of yttrium and all of the rare earth elements except promethium were prepared by Dr. Charles W. Koch and Mr. Richard J. Borg from very pure oxide stocks (similar to those described by Zalkin and Templeton[6]) by reaction with appropriate mixtures of water and hydrogen chloride vapors at elevated temperatures. Powder patterns were taken in cameras of radius 4.5 cm. with CuKα (λ 1.5418 Å.) and CrKα (λ 2.2909 Å.) radiations.

Results

The oxychlorides of the elements lanthanum to holmium have the tetragonal PbFCl type structure. The oxychlorides of thulium, ytterbium and lutetium have another structure which has not been determined. Erbium oxychloride is dimorphic, having been prepared with each of these two structures. The lattice dimensions and unit cell volumes of the tetragonal oxychlorides are listed in Table I, together with previous results. A plot of the unit cell volume as a function of atomic number is a smooth curve except for the usual cusp at gadolinium.

TABLE I

TETRAGONAL LATTICE PARAMETERS

	a, Å.	c, Å.	Vol. unit cell, Å.^{3}
LaOCl	4.119 ± 0.002	6.883 ± 0.004	116.78
	(4.117)[a]	(6.879)[a]	
	(4.121 ± .003)[b]	(6.885 ± .009)[b]	
CeOCl	4.080 ± .004	6.831 ± .007	113.71
PrOCl	4.051 ± .002	6.810 ± .006	111.76
	(4.053 ± .003)[c]	(6.800 ± .009)[c]	
NdOCl	4.018 ± .002	6.782 ± .004	109.49
	(4.04 ± .03)[c]	(6.77 ± .04)[c]	
SmOCl	3.982 ± .001	6.721 ± .002	106.57
EuOCl	3.965 ± .004	6.695 ± .007	105.25
GdOCl	3.950 ± .002	6.672 ± .004	104.10
TbOCl	3.927 ± .004	6.645 ± .007	102.47
DyOCl	3.911 ± .003	6.620 ± .006	101.26
HoOCl	3.893 ± .003	6.602 ± .004	100.06
ErOCl	3.88 ± .02	6.58 ± .06	99.1
YOCl	3.903 ± .002	6.597 ± .004	100.49
	(3.900 ± .002)[c]	(6.604 ± .004)[c]	

[a] Reference 1. [b] S. Fried, W. Hagemann and W. H. Zachariasen, THIS JOURNAL, **72**, 771 (1950). [c] Reference 2.

The PbFCl structure has atoms in the following positions of space group D_{4h}^{7} ($P4/nmm$)

2 M in 2 (c): $0, {}^1/_2, u;\ {}^1/_2, 0, \bar{u}$
2 O in 2 (a): $0,0,0;\ {}^1/_2, {}^1/_2, 0$
2 Cl in 2 (c): $0, {}^1/_2, v;\ {}^1/_2, 0, \bar{v}$

Sillén and Nylander[1] have given the parameters as $u = 0.178$ and $v = 0.635$ for LaOCl, while Zachariasen[2] has given them as 0.18 and 0.64, respectively, for NdOCl, PrOCl, PuOCl and YOCl.

Diffraction intensities were calculated for many combinations of values of u and v for both SmOCl and HoOCl. For both compounds the best agreement was found with $u = 0.17$ and $v = 0.63$. The limits of error are estimated as 0.005 and 0.01 for the two parameters. The reflections considered include l values up to 8. The interatomic distances are listed in Table II. The most interesting feature of these distances is that the two types of metal–chlorine distance remain equal (within experimental error) in spite of the very short chlorine–chlorine distance which results. That is, the anion repulsion is much less than one would expect for conventional ionic radii.

TABLE II

INTERATOMIC DISTANCES IN SmOCl AND HoOCl

Atoms	Distance, Å. SmOCl	HoOCl
M–O	2.30	2.25
M–Cl	3.09,[a] 3.11[b]	3.04,[a] 3.05[b]
Cl–O	3.19	3.12
Cl–Cl	3.31	3.24
O–O	2.81	2.75

[a] One neighbor. [b] Four neighbors.

The explanation may lie in a deviation from spherical symmetry of the chloride ion. This equality of metal–chlorine distances also occurs to within experimental error for LaOCl,[1] PrOCl,[2] NdOCl,[2] YOCl[2] and PuOCl,[2] but in these cases the anion–anion distances are not as small because of the greater cation size.

Acknowledgment.—We thank Dr. Koch and Mr. Borg for preparing the compounds and Professor Cunningham for his interest in the work. The diffraction patterns were obtained by Mrs. Helena W. Ruben. This research was supported by the U. S. Atomic Energy Commission.

RADIATION LABORATORY, DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA

An Empirical Quantitative Relationship between Structure and Molecular Rotatory Power

BY TOM R. THOMSON

RECEIVED AUGUST 5, 1953

The relationship between optical rotation and structure has been worked out in part by such well-known methods as Hudson's rules of isorotation. However, a generalized treatment either theoretical or empirical, capable of predicting the magnitude of the rotation from the constitution of the active molecule is as yet lacking. The following describes an empirical relationship that enables the rotation of at least the simpler types of optically

---

[1] L. G. Sillén and A. L. Nylander, *Svensk. Kem. Tidskr.*, **53**, 367 (1941).

[2] W. H. Zachariasen, *Acta Cryst.*, **2**, 388 (1949).

[3] W. Nieuwenkamp and J. M. Bijvoet, *Z. Krist.*, **81**, 469 (1931).

[4] C. W. Koch, A. Broido and B. B. Cunningham, THIS JOURNAL, **74**, 2349 (1952).

[5] C. W. Koch and B. B. Cunningham, *ibid.*, **75**, 796 (1953).

[6] A. Zalkin and D. H. Templeton, *ibid.*, **75**, 2453 (1953).

active molecules to be calculated with a fair degree of accuracy.

The method makes use of the *asymmetry product* of Guye and Brown[1,2] who, in 1890, related the molecular rotation, (M), to a function of four terms, in turn related to four groups attached to an asymmetric carbon atom

$$(M) = [(a - b)(a - c)(a - d)(b - c)(b - d)(c - d)] \quad (1)$$

Instead of using the masses of the groups for the four terms a, b, c and d, as did Guye and Brown, however, a different method of calculating these contributions is used, wherein the value is derived from the structure of the group, adding a contribution for each atom vectorially.

For example, a methyl group is considered as a carbon atom plus three hydrogen atoms located at tetrahedral angles with respect to the methyl carbon atom. The total effect, then, of this group would be the effect of one carbon atom plus the vector components of each of the three hydrogen atoms along the line joining the methyl carbon atom to the asymmetric carbon atom. Each hydrogen atom can be broken down into two vectors, one along this line and one normal to it. These latter vectors can be neglected if free rotation is possible, since all positions around 360° are equally probable, thus cancelling out any effect.

Bond distances need not be included in at least these simple compounds, since they are included in the values assigned to each element. This assumes, for example, hydrogen always joined to carbon; in cases where hydrogen is joined to oxygen, a slightly different value must be used.

It is also possible to assume tetrahedral bond angles for all carbons; discrepancies will appear when bond angles are strained. When compounds of other multivalent elements are encountered, then their bond angles must be considered.

From studies of homologous series it has been known that the contribution of a given atom or group to the optical rotation drops off with distance from the asymmetric carbon atom. The following comparison of the contribution of a bromine atom in the homologous series $-CH_2Br$, $-CH_2CH_2Br$, etc., as calculated according to the above method, illustrates this point in a quantitative manner.

Assuming the normal bond angle of carbon to be 109° 28′, the structure of a bromomethyl group is shown in Fig. 1.

Considering only the bromine atom, for the moment, the component of its effect along the line ss′ would be given by

$$a = \text{Br}(\cos \beta) = \text{Br}(\cos 70°32') = 0.333\text{Br} = (^1/_3)\text{Br} \quad (2)$$

Similarly, in a bromoethyl group, as shown in Fig. 2, the desired component along tt′ will be $(^1/_3)$-Br, as before, and the component of this along ss′ will be (1/3)(1/3) Br or (1/9)Br.

The contribution of bromine in any normal ω-bromoalkyl group, $C_nH_{2n}Br$, will be found to be $(1/3)^n$ Br. This one-third relationship resulting from the tetrahedral carbon atom might be called a one-third law, since the effect of a group is given by $(1/3)^n X$, where X is the basic rotational value of the group, and n is the number of carbon atoms between the group and the center of asymmetry. The validity of this relationship is evident below from the successful calculation of rotations of various molecules from their structure using this law.

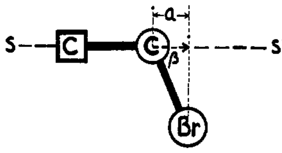

Fig. 1.

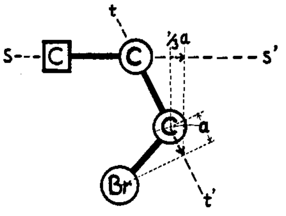

Fig. 2.

Calculation of Vectorial Contributions of Various Alkyl Groups.—On the basis of this relationship, the rotational contributions of various alkyl groups can be assigned as in Table I.

TABLE I

TABLE OF ROTATIONAL CONTRIBUTIONS FOR VARIOUS ALKYL GROUPS FOR USE IN THE MODIFIED GUYE EQUATION

Group	Expression for rotational contribution[a]
Methyl, CH_3	$C + 3(1/3)H = C + H$
Ethyl, C_2H_5	$C + 2(1/3)H + (1/3)(C + H) = (4/3)C + H$
n-Propyl, C_3H_7	$(13/9)C + H$
Isopropyl, C_3H_7	$(15/9)C + H$
n-Butyl, C_4H_9	$(40/27)C + H$
Isobutyl, C_4H_9	$(14/9)C + H$
n-C_nH_{2n+1}	$[^1/_2(3^n - 1)/3^{n-1}]C + H$

[a] The Rotational Contributions are worked out for the first two members, as examples.

Calculation of the Atomic Rotational Contribution of Carbon.—The atomic rotational constant of carbon can be found by use of equation 1, the group values from Table I, and the observed rotation values for compounds of known structure. It will be noted that if the contributions of the various alkyl groups are substituted into equation 1 since each term contains an identical hydrogen term, the subtraction of one term from the other in the equation eliminates the value for hydrogen, leaving a sixth degree equation with one unknown, which can be solved for the rotational constant for carbon.

Consider, for example, the compound methylethyl-*n*-butylmethane. Equation 1 yields the expression

$$(M) = [(1 - 4/3)(1 - 40/27)(1 - 0)(4/3 - 40/27)(4/3 - 0)(40/27 - 0)]C^6 \quad (3)$$

Substituting in the known rotation, −11.4°, for (M), and solving for C, we obtain the value of 2.50 for the atomic rotational constant for carbon.

Similar calculations on other optically active hydrocarbons of known rotation, chosen from data given by Gilman[3] and Marker,[4] yield consistent values for carbon, as shown in Table II. Only

---

(1) P. A. Guye and A. C. Brown, *Compt. rend.*, **110**, 714 (1890).

(2) P. A. Guye and A. C. Brown, *Proc. Roy. Soc. Edin.*, **17**, 181 (1890).

(3) H. Gilman, "Organic Chemistry, An Advanced Treatise," Vol. 2, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1808.

(4) R. E. Marker, THIS JOURNAL, **58**, 976 (1936).

compounds with rotations of the order of ten degrees or more were used, because the nature of the function makes too great a percentage error in the answer if the percentage uncertainty in the rotation is too large.

TABLE II

ATOMIC ROTATION CONSTANTS FOR CARBON CALCULATED FROM ACCEPTED ROTATIONS AND A COMPARISON OF THE LATTER WITH ROTATIONS CALCULATED USING AN AVERAGE VALUE OF 2.50 FOR CARBON

Compound, methane	Accepted, (M)	C	Calcd., (M)
Methylethyl-*n*-butyl-	−11.4	2.50	−11.5
Methylethyl-*n*-pentyl-	−12.0	2.47	−12.8
Methylethylisobutyl-	−21.3	2.51	−20.8
Methyl-*n*-propylisobutyl-	−14.9	2.50	−15.0
Methyl-*n*-butylisobutyl-	−11.9	2.53	−10.8
Methyl-*n*-pentylisobutyl-	− 9.3	2.49	− 9.6

Table II also includes a column of rotations calculated by use of Table I and equation 1, employing the average value of 2.50 for carbon. As might be expected from the constancy of the values for carbon, good agreement is found with the accepted rotations. This latter column is not intended as any proof of the method; the consistent values for carbon establish its validity. Rather, it is inserted merely to illustrate the proportional change in the calculated rotation when there is a variation in the value for carbon.

Calculation of Molar Rotation of Alkyl Halides.—The method is also applicable to alkyl halides. Using the same general method and a value of 2.50 for carbon, the contribution of the halogen atom can be found, and once known, the rotations of alkyl halides can then be predicted. Actually, like hydrogen the value for the halogen atom alone need not be found, but rather, the value (X–H), the difference in the values for the halogen and hydrogen, is more easily solved for and is sufficient for the calculations.

The following example will illustrate the calculation of the value (Br–H). Consider the compound bromoethylethylmethylmethane. Using the following values for the four groups in the order named: $(4/3)C + (8/9)\mathrm{H} + (1/9)\mathrm{Br}$, $(4/3)\mathrm{C} + \mathrm{H}$, $\mathrm{C} + \mathrm{H}$, H, and substituting into equation 1 and simplifying gives

$$(M) = (4C^3/6561)[36C^2(\mathrm{Br{-}H}) + 15C(\mathrm{Br{-}H})^2 + (\mathrm{Br{-}H})^3] \quad (4)$$

Using a value of 2.50 for C, the equation becomes

$$(M) = 0.009465\ [225(\mathrm{Br{-}H}) + 37.5(\mathrm{Br{-}H})^2 + (\mathrm{Br{-}H})^3] \quad (5)$$

For this particular compound (M) has the value −38.8°. Thus, the quantity (Br–H) can be found by solving the cubic equation. A graphical solution yields the value 7.40 for (Br–H).

TABLE III

A COMPARISON OF CALCULATED AND ACCEPTED ROTATIONS FOR ALKYL BROMIDES

Compound	Accepted, (M)	Calcd., (M)
1-Bromo-3-methyloctane	14.7	15.2
1-Bromo-5-methylheptane	14.9	15.5
1-Bromo-4-methylhexane	21.9	22.0

Use of this value to calculate rotations for various alkyl bromides yields good agreement with accepted values from the literature as shown in Table III.

Discussion

Though good agreement was obtained between calculated and accepted rotations in the examples presented here and in others not mentioned, notable exceptions were found. Among the alkanes and alkyl halides, these, in all cases, were compounds which, when constructed from Fisher–Hirschfelder–Taylor models, exhibited unavoidable steric hindrance. Compounds which have possible steric hindrance between groups, but which also have configurations which could avoid hindrance, showed good agreement. This seems to indicate that the criterion for applicability of this method is whether or not steric hindrance is *unavoidable*, rather than *possible*. Lack of agreement might thereby indicate unavoidable steric hindrance.

The rotations of compounds with isopropyl groups attached to the asymmetric carbon atom have for some time been known to fall out of line with the rotations of homologous series. Erroneous answers are obtained with this method in such cases. A value other than that given in Table I must be used for the isopropyl group to make the method work. Furthermore, a different value for each case is obtained, showing that the hindrance causing the error depends on the other three groups attached to the asymmetric carbon atom.

It might also be noted that reversing the assignment of groups to the four terms in the equation will result in a change of sign but not of magnitude. The method is thus applicable to predicting the rotation of either isomer and a standardization of method of choosing the order of terms is all that is needed to make the answers conform with absolute configuration.

The particular types of compounds chosen here were those purposely avoiding the many factors complicating the rotation phenomenon, such as association, solvation, hydrogen bonding, chelation, Cotton effect, etc. It is hoped that the method can be extended to include other groups, ring compounds, compounds with more than one asymmetric carbon atom, and even perhaps those with asymmetric atoms other than carbon.

DEPARTMENT OF CHEMISTRY
ADAMS STATE COLLEGE
ALAMOSA, COLORADO

The Hydrolysis of Some Alkyl Lactates I. Alkaline Hydrolysis[1]

BY KENNETH H. VOGEL AND J. C. WARNER

RECEIVED MARCH 12, 1953

The kinetics of the alkaline hydrolysis of certain normal and branched-chain alkyl acetates[2] and benzoates[3] have been studied, and the effects of lengthening and of branching the alkyl carbon

---

(1) Abstracted from a thesis submitted by K. H. Vogel to the Committee on Graduate Degrees, Carnegie Institute of Technology, in partial fulfillment of the requirements for the D.Sc. degree.

(2) H. Olsson, *Z. physik. Chem.*, **118**, 107 (1925).

(3) E. Tommila, *Ann. Acad. Sci. Fennicae*, **A59**, No. 3, 3 (1942).