

TABLE I
ROTATIONAL RELATIONSHIPS OF ALKYL HALIDES FROM
ALKYLMERCURIC HALIDES^a

(S)- (+)- <i>sec</i> -BuHgX	[α] ^{25D} (c 4, EtOH) ^b	Conditions	(S)-(+)- <i>sec</i> -BuX	
			X	[α] ^{25D} (neat) [M] ^{25D} (neat)
Br	25.8	Br ₂ , pyridine- γ-collidine, -65°	Br	33.1 45.3
Cl	26.0	Br ₂ , pyridine- α-picoline, -75°	Br	32.6 44.7
Cl	26.0	Cl ₂ , pyridine, -30°	Cl	36.0 33.3
Cl	26.0	ICl, pyridine- DMF, -10°	I	33.4 61.6

^a References 4a and 4b. ^b Actual conversions carried out with material of lower activity and then recalculated using the maximum reported value for 2-bromomercuributane (25.8°).

With the working hypothesis that the magnitude of the molecular rotation of an asymmetric screw pattern is linearly related to the refractions of the bonds making up the pattern, the bond refraction-optical rotation relationship was investigated in a number of systems.

The common bond refractions¹⁵ used in this study are listed in Table II.¹⁶ The values given are the mean of

TABLE II
COMMON BOND REFRACTIONS^a

Bond	Refraction (cm ³ , 20°, sodium D line)
C-H	1.676
C _{al} -C _{al}	1.296
C _{al} -C _{ar}	1.59
C _{ar} -C _{ar}	2.688
C=C	4.17
C≡C (terminal)	5.87
C-F	1.44
C-Cl	6.51, 6.74 in 2-chlorobutane
C-Br	9.32, 9.80 in 2-bromobutane
C-I	14.61, 14.08 in 2-iodobutane
C-O (ethers)	1.54
O-H (alcohols)	1.66
O-H (acids)	1.80
C=O	3.32
C≡N	4.82
C-N	1.57
N-H	1.76
C-Hg	7.21, 7.51 for secondary compounds
Hg-Cl	10.9 ^b
Hg-Br	14.5 ^b

^a Reference 16. ^b B. C. Curran, *J. Amer. Chem. Soc.*, **64**, 830 (1942).

a large number of compounds containing such a bond. In the interest of higher accuracy the experimental value has been used when available. If a specific value is not available, then the bond refraction for the most nearly analogous compound has been used (*i.e.*, for the *sec*-pentyl and *sec*-octyl series the bond refraction of the similarly substituted *sec*-butyl derivative was used).

(15) J. R. Partington, "An Advanced Treatise on Physical Chemistry," Vol. IV, Longmans, Green and Co., London, 1953, pp 42-72.

(16) For more complete lists, see A. I. Vogel, W. T. Cresswell, G. H. Jeffery, and J. Leicester, *J. Chem. Soc.*, 514 (1952); A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

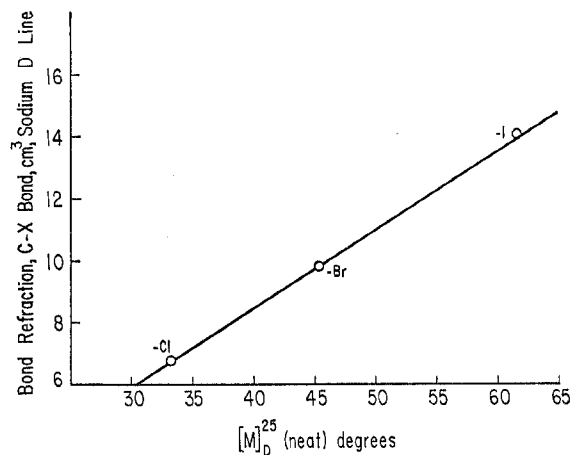


Figure 1.—Relationship between bond refraction and molecular optical rotation, *sec*-butyl halides.

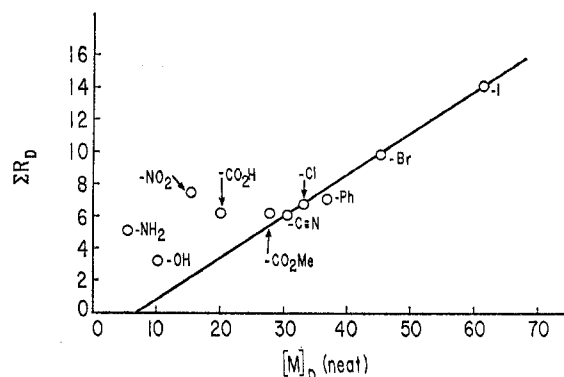


Figure 2.—Bond refraction-optical rotation correlation, *sec*-butyl compounds including nonsymmetrical substituents.

Results

In the *sec*-butyl series the alcohol, acid, and amine are easily resolved to optical purity and when plotted in a similar manner (using ΣR_D for multivalent substituents¹⁷) the points for these compounds are found to fall to the left of the line determined by the halides (Figure 2) and are not correlated.¹⁸ Since neither carboxy, amino, nor hydroxy substituents are correlated, it appears that there is a symmetry requirement for correlation. Lack of fit was observed for the nitro and phenyl groups but the methyl group does correlate, (*vide infra*) indicating that a threefold axis of rotation (which coincides with the asymmetric carbon-substituent axis) is the minimum symmetry requirement.

It is also expected that a similarity in rotamer populations is also necessary, but there are too few data available to test this aspect. For the majority of the compounds discussed here it is expected that the rotamer with the alkyl groups *trans* is heavily populated.

(17) The rotations of the alkyl-HgX (X = Cl, Br, I) indicate that the Hg-X bond also contributes to the pattern of polarizability. The influence of bonds 2,3 to the asymmetric center is a general phenomenon. The substituent bond refraction, as pertains to optical activity, is then defined to be the sum of the bond refractions surrounding the atom bonded to the asymmetric center, and denoted by ΣR . For example, $\Sigma R_D(-C\equiv N) = R_D(C-C) + R_D(C\equiv N)$; $\Sigma R_D(-HgR) = 2R_D(C-Hg)$.

(18) Points falling to the left of the line are either not correlated or not of the same optical purity as those on the line. Since it is generally accepted that Kenyon's value¹⁹ for the rotation of *sec*-butyl alcohol represents optical purity, the points falling to the left of the line are not correlated. A point falling to the right of the line indicates that it is either not correlated or that the line represents a lesser degree of optical purity.

(19) R. H. Pichard and J. Kenyon, *J. Chem. Soc.*, **99**, 45 (1911).

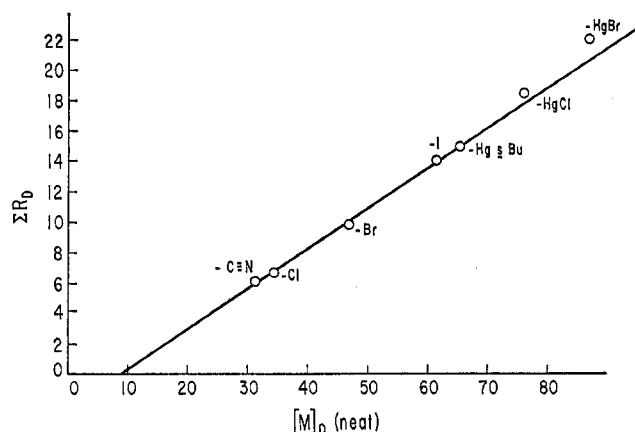
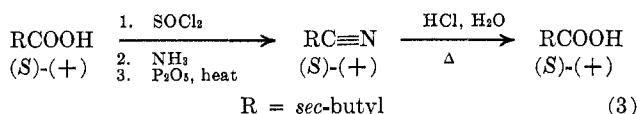


Figure 3.—Bond refraction-optical rotation correlation for *sec*-butyl compounds.

The rotation of optically pure 2-methylbutyronitrile can be determined by its relationship to 2-methylbutyric acid:



The molecular rotation of optically pure 2-methylbutyronitrile lies between 30.1 and 32.5° (see Experimental Section) and is found to correlate with the halogen substituted *sec*-butyl compounds (Figure 2) using the ΣR_D value.

Other substituents which have a cylindrical axis of symmetry, such as -HgCl and -HgBr correlate with slight deviation which may be due to a solvent effect on the rotation. All of the mercury compounds are of the same optical purity as shown by conversion reactions.²⁰

It is concluded that the bond refraction correlation is valid for substituents that possess a threefold or greater axis of symmetry which coincides with the bond axis and that the only bonds which contribute significantly to the magnitude of the optical rotation are those in the 1,2 and 2,3 positions.

The upper and lower limits, when available, of optical rotation for (*S*)-*sec*-butyl, *sec*-pentyl, *sec*-octyl, and α -phenethyl compounds are given in Table III. The correlation plots for these systems are shown in Figure 3 and 4. The equations for the lines are

$$\textit{sec}\text{-butyl } [M]_D = 3.78\Sigma R_D + 8.8 \quad (4)$$

$$\textit{sec}\text{-pentyl } [M]_D = 5.3\Sigma R_D + 15.7 \quad (5)$$

$$\textit{sec}\text{-octyl } [M]_D = 9.3\Sigma R_D - 14.3 \quad (6)$$

Because of the inclusion of effects more than one atom removed from the asymmetric center, it is reasonable to expect that the 2-methylbutyl system follows the bond refraction correlation. However, since the -CH₂X group does not have an axis of symmetry the 2-methylbutyl compounds cannot be considered as -CH₂X substituted *sec*-butyl compounds. Brauns⁷ has determined both the molecular rotation and molecular refraction for the configurationally related series 2-methylbutyl alcohol, fluoride, chloride, bromide, and iodide shown in Table IV. The chloride, bromide, and

TABLE III
ROTATIONS OF *sec*-BUTYL, *sec*-PENTYL, *sec*-OCTYL, AND α -PHENETHYL COMPOUNDS

Compd	Molecular rotation ^a , 22 ± 3°, —sodium D line—		Specific rotation, 22 ± 3°, sodium D line	Ref
	Lower limit	Upper limit		
2-Butanol	10.3	10.3	13.8	<i>b</i>
2-Aminobutane	5.43	5.43	7.44	<i>c</i>
2-Methylbutyric acid	20.2	20.2	19.8	<i>d</i>
2-Methylbutyric acid methyl ester	27.8		23.9	<i>d</i>
1-Phenyl-2-methylbutane	15.8	17.2	11.2 ± 0.5 ^e	<i>f</i>
2-Phenylbutane	37		27.6	<i>g</i>
2-Nitrobutane	15.6		15.2	<i>h</i>
2-Methylbutyronitrile	30.1	32.5	37.7 ± 1.4 ^e	<i>i, j</i>
2-Chlorobutane	33.3	35.3	37 ± 1 ^e	<i>k, l</i>
2-Bromobutane	45.4	48.4	34.2 ± 1.1 ^e	<i>k, m</i>
2-Iodobutane	61.6		33.5	<i>n</i>
Bis(2-butyl)-mercury	65.5		20.8 ^{o,p}	<i>n</i>
2-Chloromercuri-butane	76.2		26 ^p	<i>n</i>
2-Bromomercuri-butane	87.1		25.8 ^p	<i>n</i>
2-Pentanol	12.1	12.1	13.7	<i>b</i>
2-Chloropentane	46	46.5	42.5	<i>q, r</i>
2-Bromopentane	63		41.6	<i>q</i>
2-Iodopentane	92		46.7	<i>q</i>
2-Phenylpentane	25.8		17.4	<i>s</i>
2-Octanol	12.7	12.7	9.76	<i>t</i>
2-Nitrooctane	29.4	30.4	18.8 ± 0.3 ^e	<i>u</i>
2-Chlorooctane	54		36.15	<i>q</i>
2-Bromooctane	81.1		42.1	<i>q</i>
2-Iodooctane	115		47.9	<i>q</i>
1-Phenylethyl alcohol	52.3	52.3	42.9	<i>t</i>
1-Phenyl-1-chloroethane	146		103.9	<i>v</i>
1-Phenyl-1-bromoethane	178		96.4	<i>w</i>
1-Phenyl-1-chloromercuriethane	275		80.6	<i>x</i>
1-Phenyl-1-cyanoethane	-16.5		-14.5 ^v	<i>z</i>

^a All rotations in the homogenous state unless indicated otherwise. ^b See ref 19. ^c L. G. Thomé, *Ber.*, **36**, 582 (1903). ^d K. Freudenberg and W. Lwowski, *Justus Liebig's Ann. Chem.*, **594**, 76 (1955). ^e The range within which the rotation of the optically pure substance must lie. ^f See ref 6. ^g P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **100**, 685 (1933). ^h N. Kornblum, J. T. Patton, and J. B. Nordmann, *J. Amer. Chem. Soc.*, **70**, 746 (1948). ⁱ J. Kenyon and W. A. Ross, *J. Chem. Soc.*, 3407 (1951). ^j This work. ^k See ref 4a. ^l See ref 6a. ^m See ref 6b. ⁿ See ref 4b. ^o One group active. ^p *c* 4 in ethanol. ^q D. H. Brauns, *Recl. Trav. Chim. Pays-Bas*, **65**, 799 (1946). ^r See ref 23. ^s D. J. Cram, *J. Amer. Chem. Soc.*, **74**, 2152 (1952). ^t See ref 14. ^u N. Kornblum and L. Fishbein, *ibid.*, **77**, 6269 (1955). ^v R. L. Burwell, A. D. Shields, and H. Hart, *ibid.*, **76**, 909 (1959). ^w H. Dauben and L. L. McCoy, *ibid.*, **81**, 5404 (1959). ^x D. S. Matteson and R. A. Bowie, *ibid.*, **87**, 2587 (1965). ^y This compound has the opposite sign of rotation for the same configuration as the rest of the series. ^z K. Patterson, *Ark. Chem.*, **10**, 283 (1956).

iodide correlate as shown in Figure 5, the alcohol fails again, and the fluoride correlates only if the sign of the bond refraction is changed. A discussion of the mean-

TABLE IV^a
 ROTATIONS OF (S)-2-METHYLBUTYL COMPOUNDS

Compd	[M] ²⁰ _D , deg	[M] ²⁰ _D , deg	Bond refrac- tion C-X Bond	ΣR _D
2-Methylbutyl alcohol	-5.76	-5.06	-1.54	3.11
2-Methylbutyl fluoride	-8.86	-7.98	-1.49	3.16
2-Methylbutyl chloride	+1.64	+1.75	6.45	11.10
2-Methylbutyl bromide	+4.04	+6.11	10.0	14.65
2-Methylbutyl iodide	+5.68	+11.25	14.53	19.18

^a Rotations and bond refractions calculated from the data given in ref 7.

ing and validity of this sign change is given in the section on configurational relationships. The equation for the line is eq 7.

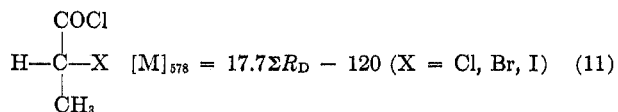
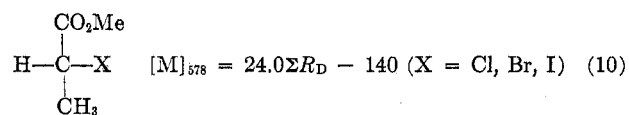
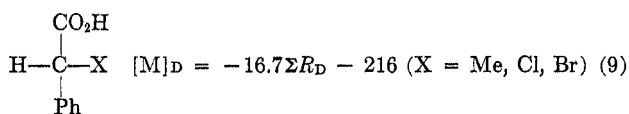
$$[M]_D = 1.2\Sigma R_D - 11.7 \quad (7)$$

The slope of the line is approximately one-third of the *sec*-butyl slope, in accord with Thomson's proposal.^{18b} Thomson's method of predicting the rotation of hydrocarbons by means of pairwise interactions considers that the contribution of a particular 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 bond refraction-molecular rotation correlation can also be applied to substituted (*R*)-1-phenethyl compounds. Figure 6 shows the data plotted in the usual manner, with the sign of the cyano group reversed (*vide infra*). The equation for the line is eq 8.

$$[M]^{20}_D = 12.3\Sigma R_D + 59.7 \quad (8)$$

Other systems for which a linear relationship has been shown between three or more derivatives include the substituted phenylacetic acids²¹ and the methyl esters and acid chlorides of 1-substituted propionic acids.²² The equations for the lines and the substituents used to determine the lines are in eq 9-11.



A large body of data is available concerning the halogen-substituted acylated sugars (*O*-acylglycosyl halides) owing to the work of Brauns.²³ Using this data for a series of ten *O*-acylglycosyl halides the bond refraction-molecular rotation correlation was applied with excellent results, Table V. The bond refraction values were those of the *sec*-butyl compounds for lack of a better model system. The slope of the lines appear to

(21) W. Klyne, in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p 93.

(22) K. Freudenberg, W. Kuhn, and I. Bumann, *Ber.*, **63**, 2380 (1937).

(23) D. H. Brauns, *Recl. Trav. Chim. Pays-Bas*, **69**, 1175 (1960).

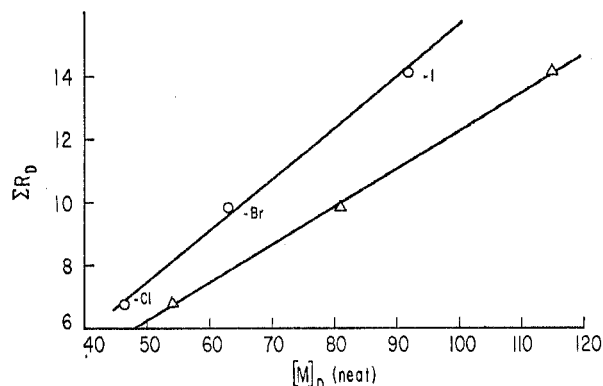


Figure 4.—Bond refraction-optical rotation correlation for *sec*-pentyl (O) and *sec*-octyl (Δ) compounds.

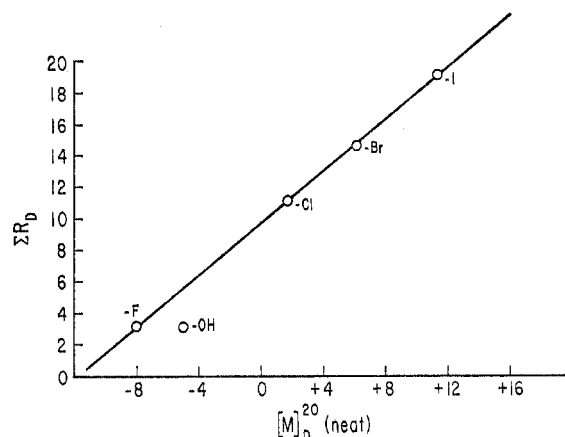


Figure 5.—Bond refraction-optical rotation correlation for (*S*)-2-methylbutyl compounds.

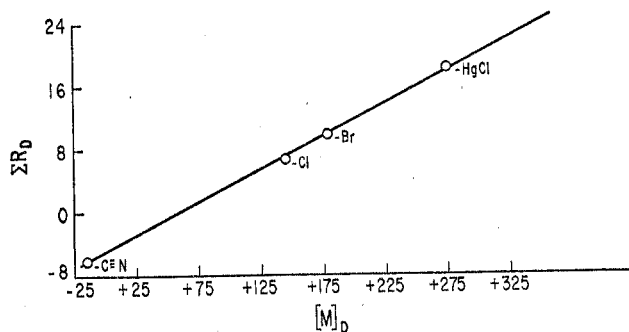


Figure 6.—Bond refraction-optical rotation correlation for (*R*)-1-phenethyl compounds.

be independent of the structure of the sugar in accord with Hudson's first Rule of Isorotation.²⁴ Other halogen-substituted sugars studied by Brauns were *p*-halosalicin and its pentaacetate, and (1-haloacetyl)tetracetyl- α -D-glucose (Table VI). For these sugars, which have the halogen substituent further removed from the asymmetric center, the slopes of the lines are smaller, in agreement with the general principles of Thomson.¹³

The bond refraction-optical rotation correlation has also been applied to the asymmetric silicon compounds

(24) C. S. Hudson, *J. Amer. Chem. Soc.*, **31**, 66 (1909).

TABLE V
BOND REFRACTION-OPTICAL ROTATION CORRELATION
APPLIED TO ACYLATED SUGARS^a

Sugar	Slope	Std devn	Intercept	Std devn	No. ^b pts
1-Halo-octa-acetyl-maltose	65.5	1.8	611	12	3
1-Halo-hepta-acetyl-melibiose	60.8	2.6	862	18	3
1-Halo-hepta-acetyl-cellobiose	59.0	2.3	95.1	21	4
1-Halo-hepta-acetyl-glucosido-4-mannose	59.1	4.1	-24.5	38	4
1-Halo-hepta-acetyl-gentiobiose	52.5	1.8	192	17	4
1-Halo-tetra-acetyl- α -D-glucose	61.6	1.8	2.5	17	4
1-Halo-tri-acetyl- β -L-arabinose	73.4	3.2	257	30	4
1-Halo-tri-acetyl- α -D-xylose	63.1	2.6	91.4	18	3
1-Halo-tetra-acetyl- β -D-fructose	-54.8	2.5	-233	17	3
1-Halo-tetra-acetyl- α -D-mannose	63.0	5.5	-50	50	4
mean slope	61.2				

^a Data taken from ref 23. ^b Equations determined by the method of least squares; all correlation coefficients greater than 0.992.

TABLE VI
BOND REFRACTION-OPTICAL ROTATION CORRELATION
APPLIED TO ACYLATED SUGARS (SUBSTITUENT NOT
DIRECTLY ON ASYMMETRIC CARBON)^a

Sugar	Slope	Std devn	Intercept	Std devn	No. ^b pts
<i>p</i> -Halosalicin	-3.88	0.12	-142	1.2	3
<i>p</i> -Halosalicin-pentaacetate	2.21	0.16	103	1.7	3
Haloacetyl-tetra-acetyl- α -D-glucose	8.53	1.0	367	6.9	3

^a Data taken from ref 23. ^b Equations determined by the method of least squares; all correlation coefficients greater than 0.992.

prepared by Sommer.^{25a} The halogen-substituted α -naphthylphenylmethylsilanes conform to the equation

$$[M]_D = 16.6\Sigma R_D + 97 \quad (12)$$

However the unsubstituted silane shows appreciable deviation. No explanation for this result is immediately evident. The pertinent data are shown in Table VII.

TABLE VII
ROTATIONS OF R₃Si^cX COMPOUNDS

X	$[\alpha]_D$, (pentane) ^b	$[M]_D$	ΣR_D^c
H	+34	+84	-3.17
F	+47	+125	-1.7
Cl	-6.3	-17.8	7.1
Br	-22	-72	10.1

^a R₃Si = α -naphthylphenylmethylsilicon. ^b All compounds of the same configuration, data taken from ref 25. ^c A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

(25) (a) L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965, p 44; (b) H. M. Walborsky and C. G. Pitt, *J. Amer. Chem. Soc.*, **84**, 4831 (1962).

Another series of compounds with atomic asymmetry are the 1-methyl-2,2-diphenylcyclopropyl halides. The rotations^{25b} of the (*S*) chloride, bromide, and iodide and the (*R*) hydrocarbon correlate to eq 13.

$$[M]_D = 52.7\Sigma R_D - 184 \quad (13)$$

Discussion

The bond refraction-optical rotation correlation corresponds to the general eq 14 where *m* is the slope,

$$[M] = m\Sigma R + I \quad (14)$$

ΣR is the bond refraction parameter as defined earlier, and *I* is the intercept rotation. A linear equation, in two terms, one substituent dependent and one substituent independent, is a direct consequence of Brewster's model.^{13a}

Kirkwood's polarizability theory of optical rotatory power^{12a} also results in a two-term equation with substituent dependent and substituent independent terms.²⁶ The bond refraction-optical rotation correlation is in general agreement with the predictions of the one-electron and many electron models of optical activity.^{12b}

Configurational Relationships.—Since a center of optical activity can be considered as an asymmetric screw pattern of refractivities, the sense of the Brewster screw determines the observed sign of rotation. Molecules with a right-handed Brewster screw,^{13a} *I*, with $\Sigma R A > B > C > D$, will be dextrorotatory.



The absolute configuration²⁷ of (*S*)-(+)-*sec*-butyl iodide, II leads to the conclusion that $\Sigma R I > Me > Et > H$, in accordance with the numerical values of ΣR as defined earlier.²⁸

For two previously mentioned compounds, 1-fluoro-2-methylbutane and 1-phenylethyl cyanide, the correlation fails unless the formal sign of the bond refraction²⁹ is reversed. This occurs when the value of the bond refraction is such that two groups have changed their relative order of refraction ($\Sigma R CH_2I > \Sigma R CH_3$ but $\Sigma R CH_2F < \Sigma R CH_3$). These compounds have the same configuration as the others in the series considered but the sense of the Brewster screw is reversed. To account for this, the sign of the substituent dependent term is changed by reversing the formal sign of the bond refraction. When three substituents change their orders of refractivities as in the case of the substituted

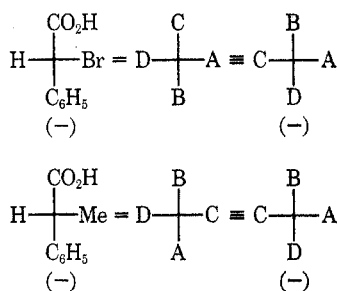
(26) A direct mathematical correspondence between the two-term equations for these three models is not implied.

(27) D. S. Tarbell and M. C. Paulson, *J. Amer. Chem. Soc.*, **64**, 2842 (1942).

(28) Although Brewster ascribes the rotations of *sec*-alkyl compounds to conformational asymmetry, analysis of these compounds by atomic asymmetry considerations gives, perhaps coincidentally, the correct answer when ΣR is used to rank substituents.

(29) Bond refractions can have either positive or negative values; however only one bond, the S-O bond, is known to have a negative value. Consequently, all bond refractions will be considered as having positive formal signs.

phenylacetic acids (eq 9) the sense of the Brewster screw remains the same, but the formal sign is still reversed. In any substitution which causes a change in the order of refractivities, the formal sign of the substituent is reversed.



The relative order of refractivities, as determined by ΣR , closely parallels the rotational rank of substituents as determined by Brewster.¹³ A comparison of ΣR and Brewsters' conformational rotatory powers is shown in Table VIII.

TABLE VIII
ROTATIONAL RANKING OF SUBSTITUENTS

Substituent (X)	Bond refractivity parameter, ΣR	Conformational rotatory power, k (C-H) (X-H) ^a
-I	14.1	250
-Br	9.8	192
-Cl	6.74	170
-C ₆ H ₅	6.98	140
-C≡N	6.1	160
-CO ₂ H	6.2	90
-Me	6.3	60
-Et	5.95	
-NH ₂	5.09	55
-OH	3.2	50
-H	1.676	0
-D	1.65	No data
-F	1.44	No data

^a Reference 13a.

The empirically derived order of ranking (from the sign of rotation for a given configuration, as determined by the sense of the Brewster screw) is I > Br > Cl > C₆H₅ > CO₂H > Me > Et > H > D > F; and C₆H₅ > C≡N > Me. This order is in good agreement with that derived by ΣR values except in the range of values 6 to 7. The deviants are those substituents which fail to meet the symmetry requirement or whose rank is determined by small differences in refraction.

Variation with Wavelength.—The bond refraction-optical rotation relationship has been examined in the range of wavelengths 434–436 nm, a wavelength at which the bond refractions are known¹⁶ and the rotation easily measured.³⁰ When the rotations of the *sec*-butyl halides and 2-methylbutyronitrile at 436 nm are compared with the bond refractions at 434 nm, Table IX, a linear relationship results; $[M]_{436} = 8.53\Sigma R_{434} + 7.6$.¹⁴ It is concluded that the bond refraction-optical rotation relationship is valid at other wavelengths when both the rotation and the refraction are measured at the same wavelength.

(30) The Zeiss photoelectric polarimeter permits the measurement of optical rotation at 578, 546, 436, 405, and 365 nm. The bond refractions are commonly determined at 656, 589, 486, and 434 nm. The difference between 434 and 436 nm is assumed to be negligible.

TABLE IX
ROTATION RELATIONSHIPS OF *sec*-BUTYL X COMPOUNDS
AT 589 AND 436 NM

(S)-(+)- <i>sec</i> -Butyl X	Observed rotations, 436/589 ratio	$[M]_{589}^a$	$[M]_{436}$	ΣR_{434}^b
-CN	1.944	31.3	60.8	6.24
-Cl	2.007	33.3	66.4	6.89
-Br	2.036	45.4	92.4	10.12
-I	2.193	61.6	135.2	14.9

^a Cf. Table III. ^b Reference 16.

Toward the *a priori* Prediction of Rotations.—The bond refraction-optical rotation correlation does not allow the complete *a priori* prediction of the optical rotation of a compound RX. It does permit, however, an accurate value of the rotation of RX to be determined if the following criteria are satisfied. (1) The substituent, X, possesses a greater than twofold axis of symmetry (considering the asymmetric atom and two positions beyond) which coincides with the asymmetric atom-substituent bond. (2) The bond refractions for the substituents are known or can be measured. (3) The correlation equation for the system R- has been determined. By far the most stringent condition is 3, since accurate data for all but a few systems are completely lacking. The theoretical prediction of the slope and intercept for any system R- is not possible at the present. For the closely related series, *sec*-butyl, *sec*-pentyl, *sec*-octyl, the slopes appear to be a constitutive function of the chain length. The slopes (m) of these systems follow the linear relationship in eq 15

$$m = 0.0984(\text{MW}) - 1.84 \quad (15)$$

where MW is the molecular weight of the chain. Other constitutive functions such as chain "size" are also applicable. This functionality allows the estimation of the slopes of the *sec*-hexyl, *sec*-heptyl, and *sec*-nonyl systems. Unfortunately there are no accurate data available for these systems.

The demonstrated applicability of Thomson's rule of $1/3^{13b}$ permits the prediction of the slopes of the 2-methylpentyl, 2-methylhexyl, 2-methylheptyl, 2-methyloctyl, and 2-methylnonyl systems to be made. Again, no accurate data are available for these systems.

There appears to be no correlation between the intercepts (I) and any obvious function, precluding the complete prediction of the rotations of the 2-substituted hexyl, heptyl, and nonyl compounds.

Predicted Molecular Rotations.—The equations derived previously for the *sec*-butyl, *sec*-pentyl, *sec*-octyl, and 1-phenethyl systems may be used with available bond refraction data to predict the rotations of previously unstudied compounds. The rotations listed in Table X are for compounds of the (S) configuration, in the homogeneous state for liquids or as dilute solutions in nonpolar solvents for solids. The estimated accuracy of these predictions is $\pm 5\%$.

The predicted value for 3-phenylbutyne (1-phenethylacetylene) is subject to some doubt because of uncertainty as to the formal sign of the acetylenic group in this compound. When the ΣR_D for two groups differ by a small amount (-C≡C-H = 7.17, -C₆H₅ = 6.97) the sense of the Brewster screw may be determined by factors other than those considered here, such as an

TABLE X
 PREDICTED MOLECULAR ROTATIONS OF (S)-RX, [M]^d

X	ΣR_D^a	<i>sec</i> - Butyl	<i>sec</i> - Pentyl	<i>sec</i> - Octyl	α -Phenethyl
-C \equiv C-H	7.17	36	54	52	-148 or 28
-C \equiv N	6.12	... ^c	48	43	... ^c
-HgR ^b	15.02	... ^c	95	125	-244
-HgCl	18.4	... ^c	113	157	... ^c
-HgBr	22.0	... ^c	132	190	-330
-CPh ₃	6.07	31.7	48	42	-134
-SiPh ₃	11.3	51.5	76	91	-199
-SiR' ₃ ^d	10.1	47.0	70	80	-184
-GePh ₃	11.93	53.9	79	97	-206
-GeR' ₃	12.2	54.9	80	99	-210
-SnPh ₃	15.5	67.4	98	130	-250
-SnR' ₃	16.6	71.5	104	140	-264
-PbPh ₃	30.9	125.6	180	273	-440
-PbR' ₃	24.0	99.5	143	209	-355

^a Bond refractions taken from ref 16. ^b One group active.
^c Known compound, see Table III. ^d R' = an alkyl group.

unusual conformational preference or significant contributions from lower wavelength absorptions.

Experimental Section

Melting points and boiling points are uncorrected. Rotations were measured with a Zeiss photoelectric polarimeter. All solvents and reagents were of the best commercial grades.

(+)-2-Methylbutyric Acid.—Using the procedure of Freudenberg and Lwowski,³¹ 40 g (0.455 mol) of 2-methylbutanol ($[\alpha]^{25}_D$ -4.04°, neat, 1 dm, K & K Laboratories) was oxidized by basic permanganate to (+)-2-methylbutyric acid. The acid exhibited bp 78–80° (16 mm), $[\alpha]^{25}_D$ +16.2° (neat); lit. bp 78° (15 mm),

(31) K. Freudenberg and W. Lwowski, *Justus Liebigs Ann. Chem.*, **594**, 76 (1955).

d^{25}_D , 0.9332. The yield was 20 g (43%). The product was diluted with racemic material for further use.

(+)-2-Methylbutyronitrile.—A mixture of 20 g (0.2 mol) of (+)-2-methylbutyric acid, $[\alpha]^{25}_D$ +4.90°, neat, and 47 g (0.4 mol) of thionyl chloride was stirred at room temperature for 5 hr. The excess thionyl chloride was removed at room temperature on a rotary-film evaporator and the remaining acid chloride added slowly to 100 ml of concentrated NH₄OH solution at -45°. The resulting amide was filtered while cold, the solid partially dissolved in chloroform and filtered to remove the insoluble ammonium chloride, and the amide precipitated by addition of petroleum ether (60–90°). The amide was filtered and dried to yield 9.3 g (40%) of (+)-2-methylbutyramide. The product was not crystallized in order to avoid optical fractionation, and was used directly in the next step.

Using the procedure of Jensen and Rickborn³² 5.9 g (0.0505 mol) of (+)-2-methylbutyramide was treated with 7 g (0.048 mol) of phosphorus pentoxide. The solids were mixed in a simple distillation flask and then placed in a vacuum distillation apparatus, in which the receiver was cooled in liquid nitrogen. A vacuum was applied and the pot immersed in a 140° oil bath. The nitrile distilled as formed and 3.7 g (88.5%) was collected: $[\alpha]^{25}_D$ +9.00° (neat); d^{25}_D 0.806, n^{25}_D 1.3955 (lit.³³ n^{20}_D 1.3900).

(+)-2-Methylbutyronitrile of +9.0 degrees rotation was prepared in two steps, not involving the asymmetric center, from (+)-2-methylbutyric acid, $[\alpha]^{25}_D$ +4.90 (neat). Freudenberg and Lwowski determined the rotation of optically pure acid to be $[\alpha]^{25}_D$ 19.8° (neat); thus the starting acid was 24.7% optically pure and an upper limit to the optical purity of the nitrile is 24.7% and a lower limit to the rotation for optically pure 2-methylbutyronitrile is 9.00/0.247 or $[\alpha]^{25}_D$ 36.3° (neat). Kenyon's³⁴ reported upper limit for the rotation of optically pure material is $[\alpha]^{25}_D$ 39.1°.

Registry No.—(+)-2-Methylbutyronitrile, 25570-03-0.

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Debromination of *meso*- and *DL*-Stilbene Dibromides by Sodium Iodide in Dimethylformamide^{1a}

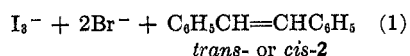
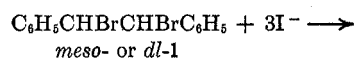
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In the sodium iodide promoted debromination of the stilbene dibromides in DMF, the *meso*-dibromide gives *trans*-stilbene while the *dl*-bromide gives both stilbenes with $[cis]/[trans] \approx 10$. The activation parameters for elimination in the temperature range of 25–60° are, for *meso*, $\Delta H^\ddagger = 16.3$ kcal/mol and $\Delta S^\ddagger = -15$ eu; for *dl*, $\Delta H^\ddagger = 22.3$ kcal/mol and $\Delta S^\ddagger = -7$ eu. At 36°, the relative rates are $k[meso]/k[dl] = 323$. A detailed estimate of the free-energy terms for solvation in DMF relative to methanol indicates that the iodide term is most important in this elimination. Sodium nitrate and lithium bromide exert a positive salt effect on the iodide reaction. As compared with methanol, the rates in DMF are larger, the spread in the *meso* and *dl* rates is greater, and the *anti* stereoselectivity of the *dl* reaction is higher: this is termed *solvent dispersion* of the rates of isomers into a *selectivity spectrum*. Our observations appear to be more consistent with stepwise ion-pair processes than with one-step dehalogenation mechanisms.

Broadly speaking, this series of papers deals with the conformational responses of a pair of diastereoisomers, the stilbene dibromides (1), subjected to a given process, elimination, under widely varying circumstances.²



Kinetic and mechanistic information was obtained for the iodide-promoted debromination of the *dl*- and

meso-1 in the standard solvent methanol.^{2c} Here, we hoped to uncover any differential conformational medium effects that might be typical of an aprotic solvent,

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