**Abstract.** Selected compounds with enantiomeric carbon centers were examined to determine the relative rotation of plane polarized light to help elucidate structural factors involved in chirality. L-valine, alanine, leucine, and isoleucine demonstrate that increasing material mass causes increased light rotation with an effect that falls roughly as the inverse square of distance from the chiral carbon. Light rotation in L-leucine and isoleucine as a function of pH suggest that positive charge increases, and negative charge decreases, light rotation. Examination of substituted secondary L-butanes revealed that polarizable nonbonding pairs appear to compete with effects of mass. A nearly perfect linear correlation was found when molar light rotation, normalized for halogen density and the square of the distance from the chiral carbon, were plotted as a function of atomic mass. This suggests that nuclear mass is the most significant contributor to light rotation that is opposed by nonbonding nucleophilic electron pairs. A negative charged carboxyl group strongly affects rotation in amino acids and lactic acid. Light rotation is not caused by selective refraction as commonly assumed but is better described as a scatter-like turn of the light plane angle.

**Introduction.** When light interacts with matter, a vast array of phenomena can occur depending on wavelength of the light and the chemical structure of the matter. Compounds with 3-dimensional asymmetric chiral atoms cause rotation of plane polarized light. Chirality is usually argued to be due to differences in refractive index that occur for oppositely rotating light waves in a synchronized pair of electromagnetic components that oscillate in a plane. However, the effect is distinct from the selective refraction caused by birefringent materials which produces circularly polarized light, rather than a new orientation of the light plane. To investigate the mechanism of chirality, the characteristics of substituents on a chiral center that cause either positive (clockwise rotation as seen by an observer approached by light) or negative rotation were examined. Several chiral compounds including selected amino acids and substituted butanes were considered to determine the relative contributions of molar mass, charge, and the presence of nonbonding electron pairs on net light rotation. A possible mechanism for light rotation by chiral compounds is discussed that causes fixed rotation but not circular polarization of the transmitted light.

**Results/Discussion.** Sodium D-line plane polarized light rotation data are evaluated to determine the effects of specific substitutions in chiral compounds. Reference rotation angles under various conditions were from the Merck Index. We first examined the effects of uncharged, nonpolar aliphatic substituents of varying mass on amino acid light rotation.

**Effects of Nonpolar Mass.** As shown in Figure 1, light rotation observed for alanine, leucine, valine, and isoleucine indicate that increasing aliphatic mass close to the chiral center causes increased clockwise light rotation in these L-amino acids. The structures are shown here.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Rotation of plane polarized light (measured in 5 M HCl) g/ml/(dl-mmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>*H₂N-C-H</td>
<td>L (+) S Alanine ( \alpha = 13^\circ ) 10²⁴/( \text{g}/\text{m}^² )</td>
</tr>
<tr>
<td>CH₃</td>
<td>5.06</td>
</tr>
<tr>
<td>COOH</td>
<td></td>
</tr>
<tr>
<td>*H₂N-C-H</td>
<td>L (+) S Leucine ( \alpha = 21^\circ ) 10²⁴/( \text{g}/\text{m}^² )</td>
</tr>
<tr>
<td>CH₂</td>
<td>9.15</td>
</tr>
<tr>
<td>CH</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
</tr>
</tbody>
</table>

**Findings on the Chemical Rotation of Light**

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Rotation of plane polarized light (squares) increases progressively with increasing mass density distribution (diamonds) of aliphatic nonpolar side groups on L amino acids. Mass density was computed by dividing the molar mass for the carbon atoms in the R group formula by the square of the distance from the chiral carbon (where 10 refers to 10 x 10^{-24} g/m^2). Single bond C-C distance from chiral carbon to first carbon in R group is 154 pM. C-C-C linear distance from chiral carbon to second C in tetrahedron is 232 pM, and C-C-C linear distance is 359 pM. M/r^2 was computed for 1) alanine as 12/1.54^2 = 5.06, 2) leucine 12/1.54^2 + 12/2.32^2 + 24/3.59^2 = 9.15, 3) valine 12/1.54^2 + 24/2.32^2 = 9.51, 4) isoleucine 12/1.54^2 + 24/2.32^2 + 12/3.59^2 = 10.45.

**Effects of Nonbonding Electron Pairs.** Light rotation caused by the chiral amino acids serine and cysteine shown below suggests that the presence of nonbonding pairs impair clockwise light rotation. Further, polarizable atoms of larger diameter appear to produce effects that compete with the effects of mass. For example, CH2OH in serine has more mass than CH3 in alanine, but rotation is nearly unchanged.

It appears that either nonbonding pairs or possibly protonated nonbonding pairs interfere with light rotation. Cysteine nonbonding pairs in larger sized, polarizable orbitals decrease rotation considerably. The sulfur radius is
100 pm with electronegativity of 2.58 Pauling units. This was investigated further and confirmed with butylamine, butyl alcohol, and halogenated secondary butanes, below and in Figure 2. Apparently the two nonbonding pairs on oxygen cause more negative rotation than the one lone pair on nitrogen does, which adds to the effect of the slight difference in mass between nitrogen and oxygen.

**Chiral derivatives of butane.**

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_3 & & \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_3 \\
\text{NH}_2 & & \text{OH} \\
\alpha = -7.6^\circ & & \alpha = -13.5^\circ \\
\text{L (+) S butylamine} & & \text{L (+) S sec butyl alcohol}
\end{align*}
\]

![Figure 2. The absolute light rotation (in degrees ml per dm mmol) is plotted against the number of nonbonding lone pairs for the substituents on secondary butane. Rotation magnitude is progressively more negative for the series NH_2 (1 lone pair), OH (two lone pairs), and Cl (three lone pairs).](image)

**Halogenated secondary butanes.** To test these hypotheses we next investigated the halogenated butanes below.

\[
\begin{align*}
\text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_3 & & \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_3 & & \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{CH}_3 \\
\text{Cl} & & \text{Br} & & \text{I} \\
\alpha = -31^\circ \text{ ml/(dm-g)} & & \alpha = -44^\circ & & \alpha = -32^\circ \\
\text{S sec butyl chloride} & & \text{S sec butyl bromide} & & \text{S sec butyl iodide} \\
= -2.87^\circ \text{ ml/(dm-mmole)} & & = -6.03^\circ \text{ ml/(dm-mmole)} & & = -5.89^\circ \text{ ml/(dm-mmole)}
\end{align*}
\]

Polarizable nucleophilic nonbonding pairs in the larger bromine orbitals compared to chlorine appear to cause more counterclockwise light rotation. The large mass of iodide may counter this effect by also increasing the clockwise rotation. The bond lengths are 127, 194, and 214 pm for C-Cl, C-Br, and C-I. Thus in C-X covalent bonds, the chloride radius is closer to the 167 ionic radius than to the 100 pm atomic radius, bromide is intermediate between 115 and 182, and iodide is closer to 140 than 206 due to differences in electronegativity and sharing. The volumes of the halogens bound to carbon are thus comparable while mass density increases from Cl\(^-\) to I\(^-\). Intact atom radii are 100, 115, and 140 for Cl, Br, and I, Ionic radii are 167, 182, 206 for Cl\(^-\), Br\(^-\) I\(^-\). Electronegativity values are 3.16, 2.96, 2.66. The data for all the substituted butanes are summarized in Figure 3.
Figure 3. Absolute light rotation in degrees mL per millimole-dl (squares) plotted as a function of molar mass (x10, where 3.5 refers to 35 g/mole) for NH₂ (1 lone pair), OH (two lone pairs), Cl (three lone pairs), Br (three pairs) and I (three pairs) substituted butane. Rotation magnitude is progressively more negative for the series with 1, 2, and 3 nonbonding pairs but reverses course to become less negative for I with far larger mass. C-N and C-O bond lengths are 147 and 143 pm. Electronegativity of N and O are 3.04 and 3.44 Pauling units, and covalent radii are N 65 and O 60 pm.

To determine if molar mass would explain the competing effects of a given number of nonbonding electron pairs, a plot of degrees rotation per mole divided by atomic mass density and the square of the bond length for the halogen substituents was constructed as in Figure 4.

Figure 4. Light rotation (counterclockwise) per mole for sec butyl chloride, bromide, and iodide (left to right) were normalized by dividing by the density of the halogen (amu per atom divided by computed spherical volume inÅ³) and the square of the C-X bond length, plotted as a function of atomic number where 0.1 refers to 0.1 x 10³⁰ g/m³ per m². The volumes of the halides were computed by estimating the radii of the halogen atoms involved in the covalent C-X bond using known electronegativity differences as a fraction of the range between atomic and ionic radii. Chloride has a higher electronegativity and thus in a shared covalent system occupies a volume closer to that of ionic chloride compared to bromine and iodine, which are less electron-withdrawing in a covalent system. The possible radii for chlorine atoms in covalent systems range between that of the atom in elemental chlorine gas (100 pm) to that of the free chloride ion (167 pm). The radii for bromine (115 pm) and iodine (140 pm) atoms as elements are also within this range. The volumes employed were estimated by using the C-X electronegativity differences to interpolate the expected volume between the extremes in range for each halogen. All were comparable and thus the atomic mass largely determined the densities. Densities were divided by the square of the published C-X bond lengths.

Molar rotation magnitudes were normalized by reporting as a function of volume of the varied substituents and the square of the bond lengths plotted as a function of atomic mass. This produced a linear relation between atomic number and extent of light rotation with a high correlation.

**Charge Effects.** Removal of a hydrogen ion produces a negative charged carboxyl and decreases clockwise light rotation of L-isoleucine shown below.

\[
\begin{align*}
\text{COOH} & \quad \text{COO}^- \\
^+\text{H}_2\text{N}-\hat{\text{C}}-\hat{\text{H}} & \quad ^+\text{H}_2\text{N}-\hat{\text{C}}-\hat{\text{H}} \\
\text{H}_3\text{C}-\hat{\text{C}}-\text{CH}_3 & \quad \text{H}_3\text{C}-\hat{\text{C}}-\text{CH}_3
\end{align*}
\]

L (+) S, S isoleucine pH = 0.2 \quad \text{L (+) S, S isoleucine pH} = 5 \quad \text{L (+) S, S isoleucine pH} = 13
\alpha = 40^\circ \quad \alpha = 11.1^\circ \quad \alpha = 11.3^\circ
\begin{align*}
\text{c = 4.6} & \quad \text{c = 3.3} \quad \text{c = 3}
\end{align*}
Similar results have been reported for L-alanine, where $\alpha = 13^\circ$ for the cationic form and $2.4^\circ$ for the zwitterion. For L-leucine $\alpha = 21^\circ$ for the cation and $\alpha = 7.6^\circ$ for the anionic form. A substantial such effect has been reported for lactic acid. L(+)-lactic acid has a specific rotation of +2.6$^\circ$ while for lactate it is -8.2$^\circ$. It is not known if these effects of elevated pH are due to removal of the hydrogen atom, the appearance of a negative charge, or the exposure of an additional lone pair on oxygen. If the negative charge is most involved in the effect then an examination of change in $\alpha$ with pH would show a larger shift for leucine above the pKa of the carboxyl group. If it is the removal of a positive charge then the larger shift would occur above the pKa of the amine group. To discern the difference, it is instructive to examine the known rotation data observed for isoleucine as a function of pH shown in Figure 5.

![Figure 5. Specific rotation for L-isoleucine as a function of pH over the range 1.8 to 12.3. For isoleucine the -COOH pKa = 2.36 and the -NH$_3^+$ pKa = 9.68. The first form I contains -COOH and -NH$_3^+$ (overall +1 charge). The second form II contains -COO and NH$_3$ (neutral Zwitterion). The third form III contains COO and NH$_2$ (overall -1 charge).]

These data suggest that the decrease in rotation magnitude in the amino acid isoleucine as pH rises due to deprotonation is chiefly caused by creation of the excess negative charge. Both I $\rightarrow$ II (large change in $\alpha$) and II $\rightarrow$ III (no further change in $\alpha$) involve loss of a proton and exposure of a nonbonding lone pair, but only I $\rightarrow$ II creates a negative charged group. II $\rightarrow$ III also removes a net positive charge which is ineffective. This change in rotation magnitude caused by deprotonation is well known for lactic acid. It appears to be the creation of the carboxylate charge in lactate, rather than deprotonation or exposure of a lone pair per se, that is responsible for the effect (Figure 6).

![Figure 6. The paths of two oppositely spinning light waves through lactic acid, clockwise and counterclockwise curves both meet at the chiral carbon. Clockwise paths begin at the methyl and progress to the left then right substituents on the chiral carbon and then to the carboxyl. Counterclockwise paths progress from the methyl to the right then left groups on the chiral carbon and then the carboxyl.]

Any compound with tetrahedral asymmetry and four unique substituents, different travel paths for the two coils affect the rotating components oppositely. By experiment, the preferred coil of electron oscillations caused by interior rotating light component fields is clockwise in L lactic acid which contains the intact electron-withdrawing carboxyl group. This causes the righthanded rotating light component in the propagation direction to interact with the coil to be impeded while the lefthanded rotating component rotation is increased. In L lactate ion, the preferred arrangement is the counterclockwise coil. The idea that the electron-donating carboxylate anion can cause this reversed effect is analogous to the fact that elemental uncharged fluorine for example is the most electronegative element on earth, but the fluoride anion has no electronegativity at all and instead seeks positive charges.

Of course interchanging any two of the substituents in D lactic acid to form L lactic causes net rotation of the same magnitude but in the opposite direction. The coil path, from methyl to hydroxyl, to hydrogen to carboxyl, changes from methyl to hydrogen to hydroxyl to carboxyl. As with L lactic/lactate, the D lactate carboxylate ion produces a
lethanded preferred coil of electronic oscillations, so the lethanded component is impeded compared to the righthanded. Rotation for light approaching an observer is dextrorotatory for L lactic and D lactate but levorotatory for L lactate and D lactic.

In the case of chiral carbon molecules, the data taken together suggest that a spiral arrangement uncharged mass (with positive nuclei and surrounding electrons) increase light rotation, while polarizable nucleophilic “nonbonding” electron pairs and net negative charges oppose this effect and cause increased rotation in an opposite direction. A very good linear correlation was found ($r^2 = 0.999$) when light rotation, normalized for the density and distance from the chiral carbon for the halogen substituents, is plotted as a function of atomic number. This suggests that the nucleus with the bulk of the mass of the substituent is involved in rotation of light that is opposed by electron pairs and also by net negative charge. The mass effect is not due to nuclear magnetic moment since all halogens have an odd number of protons but carbons have an even number while both increase rotation as a function of increasing mass number. It may result from electromagnetic fields associated with the mass and its surrounding locally jostling bonded electrons. Experiments with additional substituents and with other atomic chiral centers are necessary to test and extend these hypotheses. Since D absolute configurations rotate light the exact opposite of the corresponding L configurations, mass decreases and negative charge or nonbonding electron pairs would increase counterclockwise rotation in these cases.

**Mechanism.** Maxwell’s description of Oerstad and Faraday’s laws indicate that a variable magnetic field creates around itself an electric field with circular closed field lines. Thus changing magnetic fields associated with EM radiation induce electron currents perpendicular to the field as in loop antennae. And oscillating electric fields induce electron oscillations as in linear antennae. Thus rotating light propagating forward induces complex coil-like electron oscillations in coiled structures. It is possible to describe a mechanism by which polarized light may be rotated by chiral compounds without causing phase shift differences and circular polarization. In Figure 7 a photon of light traces out a sinusoidal pattern of electric field amplitude shown by a curved arrow while passing through a chiral compound at speed $c$ in the propagation direction.

**Figure 7. Path of a light photon passing through a chiral molecule.** The substituent depicted at left center is first passed by the photon which traces an EM field path indicated by the arrow. The substituents on right and left are above the surface plane by the Fischer convention. The angled straight lines are vertical planes drawn in front of each substituent. The second substituent passed is below the plane at lower center. The third substituent passed is at right center above the plane, and the final substituent is below the plane at upper center. Since each of the four constituents have a different electric field strength and direction, the arrangement may be compared to a helix of DNA, or a righthanded threaded hole for a righthanded threaded bolt. The component of a photon that spirals with a given handedness may pass through the system with a perturbation (due to the structure of the chiral compound) opposite to that for the opposite-rotating component. The strong covalent bonds in which electrons resonate oppose distortion and cause more resistance to rotation for one component than another because of the tetrahedral arrangement of distinct substituents in a coil.

Light rotation involves circular, or rotational, deflection of components while traveling through the sample of chiral material. The emitted light remains plane polarized, so the effect is not due to differential refraction as commonly argued. Simply, the average orientation of the electric field is rotated compared to the incident light. Note that most photons passing through a chiral sample are not rotated. Photons that pass near the chiral center however are rotated as long as the amplitude of the electric and magnetic fields physically are near or within the coil region while passing through the sample. The overall rotation observed is a statistical average of all photons passing through with a distribution of rotation magnitudes. Photons experiencing maximum rotation are directed along a coil
direction. Other entrance angles would produce a smaller rotation. Although rotating surfaces or molecules have been reported to induce Doppler-like shifts in reflected light frequency due to effects on the spin angular momentum of the light, this effect is different than chiral rotation. Molecular rotational frequency in solution is on the order of \(10^6\) seconds which is far longer than the miniscule time for a photon to pass completely through a molecule (\(10^{15}\) s). Indeed, light rotation per gram occurs in crystalline sucrose similar to sucrose tumbbling in solution.

Each substituent in the chiral compound has a proton rich center. Since electrons travel in clouds surrounding the positive nucleus, net local electric field vectors then point outward from the substituent nuclei that attract electrons from adjacent substituents. If there are four unique substituents, the overall effect is that of a coil of wire where rotating light photons can cause electron oscillations along the spiral coil. For a chiral compound, four non-identical substituents produce fields of unequal magnitude arranged as in a skewed coil of wire as shown with the curled line. Like turning a bolt in relation to a threaded hole, the magnetic and electric fields in spiraling light components induce electron oscillations along the spiral as an oscillating current in a coil. The handedness of the coil is determined by the nature of the substituents, having differing electronegativity, polarizability, asymmetry, charge, mass, and other features. The induced fields impede rotation of one light component and enhance rotation of the component rotating in the opposite direction. The plane of polarization rotates accordingly. For light approaching the compound from the opposite direction, the rotation effect is the same because a right-handed coil is right-handed regardless of direction of approach.

If any two of the four substituents are identical, then this acts as an insulator, like inserting a piece of rubber into a coil, which prohibits the unique electron oscillations along a net coiled direction. In this way, achiral compounds do not rotate plane polarized light. As pointed out earlier, a single plane of symmetry prevents chirality.

Mass increases rotation magnitude while lone pair density and negative charge oppose this effect. The rotation per molecule for one photon is small but extremely fast. In a 0.1 meter travel path, for 589 nm sodium D-line light, there are 1.7 \(8\) wavelengths of travel for any particular photon. Light enters and exits chiral compounds while remaining linearly polarized and coherent, with the same rotation rate for both right and left spinning components. The detected light has a constant single rotation value that appears to compare with a collision affecting both components together so the plane of polarization is rotated from the original normal plane. The effect seems small but is dramatic, occurring while the light is present for less than a femtosecond.

The net electric field may be thought of as colliding against the walls of the spiral compound, causing a shift in the rotation direction without affecting the forward propagation direction. Light has no mass and thus is not influenced by gravity but can be reflected, refracted, or scattered by matter. Here, light rotation is affected by nearby electric and magnetic fields that assymmetrically surround chiral centers. There are counterparts to this that are well known. Right circularly polarized light after reflection on a mirror returns in the opposite direction as left polarized and vice versa. The collisions due to interaction of light with the fields around the material mirror causes reversal of propagation direction but the rotation direction is actually conserved. Also non-polarized light is composed technically of individual polarized components all oriented in random orientations. When this non-polarized light strikes a flat reflective surface, the light becomes polarized by rotation of those out of alignment with the surface to become aligned with it. Similarly, for linear polarized light passing through chiral compounds, deflections of the electric field plane occur in a circular direction, while the propagation direction is conserved. The light is not reflected to spin in the opposite direction, but rather is merely deflected circularly. The longer the chiral path, the more the circular deflection occurs.

If the effect were due to differences in refractive index between the two spiral paths, then wavelengths (\(\bar{\lambda}_L = \bar{\lambda}_0/n_{L}\) and \(\bar{\lambda}_R = \bar{\lambda}_0/n_{R}\)), and speeds (\(v_L = c/n_L\) and \(v_R = c/n_R\)) are different for the right dextro and left levo components. The frequencies \(f\) for each would remain the same, \(f_L = v_L/\bar{\lambda}_L = (c/n_L)/(\bar{\lambda}_0/n_{L}) = f_0 = v_0/\bar{\lambda}_R = (c/n_R)/(\bar{\lambda}_0/n_{L}) = c/\bar{\lambda}_0\), determined of course by the source independent of the changes on wavelength induced by matter, as would be the rotational rates, \(\omega_L = 2\pi v_L/\bar{\lambda}_L = c/\bar{\lambda}_0\) and \(\omega_R = 2\pi v_R/\bar{\lambda}_R = c/\bar{\lambda}_0\). To remain coherent and in phase however, one component cannot have a different wavelength than the other for the same path length. So if it were refraction alone, the differing wavelengths would have to be retarded and out of phase with the other and would form circularly polarized light.

The photon is an infinitesimal point of space far smaller than a mass-containing electron, where light has no mass and is not subject to gravity. The mass effect reported here is due to electric and magnetic fields that emanate from the substituents which all are composed of proton centers and electron rich surroundings. Neutral uncharged substituents exert a given rotational effect due to interaction of electric and magnetic light fields with electric and
magnetic fields on the neutral substituents that light passes through, where the energy of the electric field in light is far larger than the magnetic field energy. The presence of nonbonding electron pairs, with localized partially negatively charged regions, oppose the effect of uncharged mass. Additional experiments to address the additive effects of these fields would be to examine equimolar mixtures of compounds having a mass effect with compounds containing nonbonding pairs.

Light is formed from electronic energy transitions and thus consists of a packet of electromagnetic energy, an electric field that oscillates in synchrony with an induced magnetic field. But essentially infinite numbers of photons irradiate a sample at any time, all in various phases. The dimension in space over which the field amplitude penetrates is usually not known. Light rotation gives us a clue as to the size of this field amplitude dimension. Chiral compounds of varying sizes might be a possible tool to investigate amplitudes of these electric field oscillations. For example, chiral compounds of tertiary substituted sulfur are known, which means that the fourth asymmetric unit on this central atom is its own lone electron pair. The size of the involved orbital is far larger than that for the nitrogen atom, where significant chirality is not recognized for tertiary asymmetric amines. For sodium D-line light of 589 nm the amplitude is such that significant rotation of the electric field plane occurs when passing through a chiral sulfur with a lone pair (atomic radius of 1.1 Å) or a chiral carbon molecule (C-C bond length 1.33 Å) but rotation is not significant for an asymmetric lone pair on nitrogen (atomic radius 0.75 Å) with a much smaller magnitude charge separation dipole. It is likely that the dimensions of the asymmetric spiral must be a substantial fraction of the field amplitude generated by the oscillating photons passing through. Additional experiments with quaternary amines of varying size and with chiral derivatives of long chain length would investigate this possibility.

References.


Figure 8. Depiction of photons produced from Na lamp before and after passing through polarizer and polarimeter. Photons are represented theoretically as frozen at an instant in time with varying electric field amplitudes (lengths of arrows). Some arrows can represent paired photon electric field planes in various orientations. Next the polarizer allows passage of those plane polarized photon pairs that orient along the polarizer axis. After passage through the polarimeter chiral solution, the field planes are variably rotated in those photons passing within asymmetric molecular coils while some pass through without rotation. The longer the polarimeter the lower the percentage of photons that pass through without rotation. The detector reports the average angle $\alpha$ of all rotations in the sample of photons.