A Correlation of the Refractive Index to the Melting Point and Molecular Weight of Some Organic Compounds.

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In a recent paper\(^1\) evidence was presented to show a relationship of the melting point to the refractive indices of some organic compounds. An explanation of this behavior was not proposed at the time of writing. This behavior can be explained.

The velocity of the light on travelling through a crystal is dependent on the atoms, ions, or groups present and their position occupied in the lattice. The ratio of the velocity of light in a vacuum compared to the velocity of light in a specific medium is termed the refractive index.

The electrons and nuclei in any molecule are mobile to a certain extent. When any non-polar or polar molecule is placed in an electric field, there will be a small displacement of the center of gravity of the electrons and nuclei. An induced dipole results in addition to a dipole that may already be present. The dielectric constant is a measure of this displacement.

Visible light, assumed to be electromagnetic, has the power of displacing only the electron shell. That is, visible light causes only a deformation of the electron cloud of any atom, ion, or group. The refractive index is a measure of the ease of the deformation of the electron cloud. Maxwell\(^2\) derived a relationship of the refractive index for light of long wave length to the dielectric constant:

\[
e = n_\infty^2.
\]

This relationship is close when the molecules are far apart. The refractivity is largest for atoms or ions with a large and loosely bound configuration. This may be illustrated by comparing the molecular refraction equivalents of the halides\(^3\): F\(^-\), 2.5; Cl\(^-\), 9.0; Br\(^-\), 12.6; and I\(^-\), 19.0. In ionic compounds the anions contribute overwhelmingly to the refractive index, since the electron cloud of the cations is small and
tightly held. The ease of deformation of the electron cloud is proportional to the cube of the radius of the ion, molecule, or atom.

The melting point of organic solids is a function of the intermolecular forces of attraction. With reference to the aliphatic dibasic acids one may conclude that packing is closer for the acids containing an even number of carbon atoms. The refractivity is proportional to the number of molecules per unit volume.

The reflectsivity of some solids and their molecular weight can be made. A study revealed that the average refractivity of uracil derivatives increased in the following order: uracil, 5-chlorouracil, 5-bromouracil, 5-iodouracil, 2-thio-5-iodouracil. The order is as predicted from the molar refraction equivalents.

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The first three compounds mentioned show negative birefringence. The axial angle for these compounds is large. The last two compounds show positive birefringence. The axial angle for iodouracil is medium, and it is small for thioiodouracil. These factors aid in the explanation of the deviation of a gradual increase in the value for \( \beta \). The numerical values for \( \alpha \), however, increase as the molecular weight increases.

In unsymmetrical structures the distortion of the electron cloud varies with the direction of propagation of light. Therefore, the velocity of the light varies with the direction of propagation. Such structures show double refraction. The magnitude of double refraction (birefringence) and the optic sign has been used in predicting molecular orientations.

Consider the unsymmetrical structures as being planar. The refraction of polarized light will be greatest when the light vibrates in the plane of the structure. Two high and comparable indices of refraction are expected for light polarized in the plane of the group. A much lower index of refraction is expected for light vibrating perpendicular to the planar structure. If the crystal contains planar molecules or groups with all their planes parallel, a large negative birefringence is expected. Examples of this class are diketopiperazine, hypoxanthine nitrate, and sodium nitrate. Cleavage, perpendicular to alpha, is usually excellent as evidenced by hypoxanthine nitrate and the micas.

If the planar groups are not parallel to each other but are parallel to a direction, large positive birefringence is expected. The highest index will parallel the direction. Benzene, iodouracil, and urea are