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A HYPOTHESIS ON THE INTERACTION BETWEEN PERMANENT MOLECULAR QUADRUPOLES AND POLARIZED PHOTONS

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Synopsis

It is assumed that a photon has an electrical field vector rotating in a plane perpendicular to its direction of propagation and a magnetic field vector in the same plane perpendicular to the electrical one. The hypothesis is based on the discovery in 1931 by A. Kastler and other scientists that radiation can exchange angular momentum with matter. When now a photon traverses molecules which contain pairs of screw-like arranged permanent dipoles the electrical vector becomes twisted according to the chirality of the screw.

The hypothesis is tested on substances whose absolute configuration is known from other sources. In cases where there is no doubt about the chirality of the molecular quadrupole, *e.g. iso*-serine, the results concerning the connection between configuration and sense of optical rotation turns out to be correct. In other cases, *e.g.* serine, nothing definite can be said at present.

Application of the method to 1,2 XX-cyclohexane (X = OH or COOH) leads to a *cis-trans* assignment of the isomers which agrees with that arrived at in a preceding paper in these communications and disagrees with the currently accepted one.

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In a theoretical investigation based on the then existing knowledge of quantum theory EINSTEIN(1) proved, in 1917, that radiation could exchange translational momentum with molecules. This lead him to designate the radiation as a "Nadelstrahlung". He even went so far as to state that "Kugelwellen gibt es nicht". His views were later confirmed experimentally by the discovery of the Compton-effect and it became custumary to denote the radiation corpuscles as photons.

In 1931 a number of authors, among which were the Nobel Prize winners A. KASTLER(2,3) and C. V. RAMAN(4), interpreted well established experimental evidence as meaning that photons not only had translational but also angular momentum. KASTLER and O. R. FRISCH(3) found, independently of each other, that the angular momentum had a component in the longitudinal direction but none in the transversal direction. To the writer this seems to make it natural or even necessary to assume that photons are endowed not only with mass as stated by EINSTEIN and confirmed by Compton's experiments, but that they also have some kind of structure.

As a reasonable structure the writer ventures to propose the following hypothesis: A photon posesses an electric field-vector which is perpendicular to its direction of propagation and rotates around that direction. It is therefore supposed to describe a screw surface which corresponds either to a right-handed (*d*-) or to a left-handed (*l*-) screw corresponding to the two kinds of circular polarized light. The pitch of the screws equals the wavelength of the light in question. Ordinary light is then considered to be a random mixture of *d*- and *l*-photons. In circular polarized light one of the two kinds is suppressed more or less completely. In linear polarized light *d*- and *l*- photons are pairwise coupled to each other so that the phases of their electrical vectors are always symmetric with respect to the plane of polarization. In stead of that one may just as well consider linearly polarized light as composed of photons whose electric field vectors are always in the plane of polarization and perpendicular to the direction of the light-ray, while their amplitudes oscillate. It should be remembered that the wavelength of light ordinarily used in polarimetry is roughly one thousand times as large as the cross sections of ordinary molecules. It follows from this that the phase of the rotating or oscillating electric field vector should remain nearly unchanged during the passage of a photon through a molecule provided that they do not interact with each other during the passage.

It should also be remembered that a photon can only interact with dipoles having vector-components perpendicular to the direction of its propagation. This follows from the circumstance mentioned above that it can only exchange angular momentum with the surroundings in the longitudinal but not in the transversal direction. This same circumstance makes the socalled Fischer-projection particularly well suited for discussions of the sense of optical rotation of molecules with one socalled asymmetry centre.

When now photons belonging to a linear polarized light ray pass a molecule which has a permanent dipole they may be exposed to orientating forces from the dipole and may exchange angular momentum with it. If, however, the ray has a macroscopic cross section and impinges on an ensemble of polar molecules performing independent rotational Brownian movements the orientating forces from the individual molecyles must cancel each other if the dipoles have not been regimented by an electrical field from the outside. Thus in case of molecules with only one permanent dipole there will be no net rotation of the plane of polarization when the ray passes the ensemble.

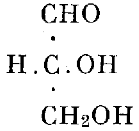
In the case of molecules which contain quadrupoles or, as we may also say, pairs of dipoles, the situation is different. We consider a dipole as a vector which points against the negative end of the dipole. A dipole around a carbon atom arises when negative electricity is displaced from the electronic cloud of an electropositive group or atom through that of the C atom unto the electronic cloud of the electronegative group or atom. This means that the vectors we have to consider roughly coincide with the edges of the classical tetrahedron. Thus, even in the case of only one asymmetric C atom, there may be two dipoles in a distance from each other. Such a pair of dipoles may be said to have the chirality of a lefthanded (*l*-) or a righthanded (*d*-) screw. The line which is perpendicular to both dipoles is the screw axis and from a figure it is easily seen whether the chirality is *d*- or *l*-. If now a photon belonging to a linear polarized ray of light traverses such a molecule its electric field vector must be twisted to the right or to the left according to whether the chirality of the quadrupole is *d*- or *l*-. But this means also that the plane of polarization is twisted either to the right or to the left. In the former case the molecule is, by convention, designated as laevorotatory or (–), in the latter one as dextro-rotatory or (+).

The twist caused by permanent screw-like quadrupoles depends on the orientation of the screw axis relative to the direction of propagation of the photons or, which is the same, the direction of the light-ray. If the former is perpendicular to the latter the twist must be zero. But if the screw axis of the quadropole is orientated in parallel to the direction of the ray the twist has its maximum value, which is the same and has the same direction whether the photon enters the molecule from one end of the screw-axis or from the other. This means of course that there is no compensation of the twisting forces when a ray of macroscopic cross section impinges on an ensemble of molecules whose screw-like quadropoles are orientated at random, which they must be when the quadrupoles are fixed relative to the skeleton of the molecule in the solution or in the gas in question when it is diluted enough to make the intermolecular forces to be of no account.

Some years ago J. H. Brewster(6) proposed "a useful model of optical activity" suggesting that a center of optical activity can usefully be described as a screw pattern of of electron polarizability. Patterns which can be described as left-handed screws are dextrorotatory (in the visible). He also presents empirical rules for predicting the rotatory effect of asymmetric atoms and conformations. To the present writer there is no doubt that patterns of polarizability may contribute to the optical activity of an asymmetric molecule, but it seems to him to be natural to compare the situation with that met with in the case of dielectric constants where both the permanent polarity and the polarizability of the molecule contribute to the polarization, the former one by orientation of the entire molecule in the electric field applied. Furthermore, Debye(7) and his numerous coworkers and followers have found by experience that so soon a molecule has a dipole-moment which can be estimated with reasonable accuracy the polraization by orientation outweighs the polarization by internal displacement of electrical charges due to the electrical field applied.

It seems therefore probable that, in cases where screwlike distinct quadrupoles are known to exist in the molecule, these must be assumed to be the main cause of the optical activity. It is only when it can be concluded from the constitution of the molecule, that the groups surrounding the active center cannot give rise to any sensible permanent quadropole that the pattern of polarizability can yield the main contribution to the rotation of the plane of polarization.

It follows that only in cases where both pairs in the quartet of groups around the asymmetric carbon atom are known to be or can be seen to be dipoles will it be possible to predict the sense of optical rotation of the molecule. There may also be cases where intramolecular displacement of atoms or of ions tend to blur the result. But in clear-cut cases, where the dipole-moments of the two dipoles in the screwlike quadropole are distinct the predictions of the model are unambiguous and have been found to agree with knowledge concerning absolute configurations obtained from other sources. In the following a few samples shall be discussed. As well known E. Fischer's arbitrary convention concerning the absolute configuration of glyceric aldehyde has for many years served as basis for the assignment of configurations to carbohydrates and also to a number of other organic compounds which can be prepared from that aldehyde without change of configuration. When the formula is written as (I)



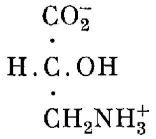
$$\begin{array}{c} \mathrm{CHO} \\ \cdot \\ \mathrm{H.C.OH} \\ \cdot \\ \mathrm{CH_2OH} \end{array} \qquad \text{(I)}$$

where the ligands in the horizontal line are meant to be located above the plane of the paper and those in the vertical line below the same plane, the molecule is said, according to Fischer's convention, to be a D-form. Fischer's glyceric aldehyde was dextro-rotatory, and this fact together with the assumption that the OH group is to the right is nowadays expressed by means of the symbol D (+). Many years after Fischer's time Bijvoet(8) and coworkers determined, by X-ray crystallography, the absolute configuration of sodium-rubidiumtartrate and thereby also that of glyceraldehyde.

Their result was that, fortunately, Fischer's convention was a true expression of the facts.

The question is, does the hypothesis discussed here yield the same result? The horizontal dipole in the D-form (I) points to the right if the direction from the positive to the negative end of the dipole is taken to be its direction. The vertical dipole is composed of two which both point outwards from the middle. According to measurements the moment of the CHO group is about $2{,}7 \; 10^{-18}$ electrostatic units or 2,7 D while that of the alcoholgroup is about 1,7 D. Consequently the vertical dipole points upwards. When therefore the electric fieldvector of a photon traverses such a molecule it will be exposed to a pair of shearing forces with tend to twist it to the left and this will be the case whether the photon enters the asymmetric molecule from one end or from the other. Outside the asymmetric molecules the fieldvector may also be twisted but the 'twist'' resulting from interaction with asymmetric or symmetric molecules must necessarily be zero by compensation as the directions of similar dipoles must be distributed at random. The plane containing the directions of the light-ray and the electrical vectors of the photons, which is the plane of polarization, must therefore as a result of all these forces be twisted to the left and the substance is then said to be dextro-rotatory or (+) in agreement with Bijvoet's result.

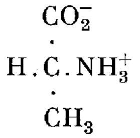
As another example we may mention *iso*serine. According to N. BJERRUM(9) it is:



$$\begin{array}{c} CO_2^- \\ \cdot \\ H.C.OH \\ \cdot \\ CH_2NH_3^+ \end{array} \qquad (II)$$

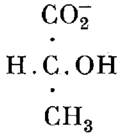
(II) shows that D-*iso*serine is D(+), in agreement with information from other sources(10).

Similarly, D-Alanine is (III)



$$\begin{array}{c} CO_2^- \\ \cdot \\ H.C.NH_3^+ \\ \cdot \\ CH_3 \end{array} \qquad (III)$$

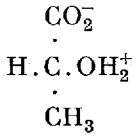
In (III) the negative end of the horizontal dipole points to the left, which shows that D-alanine is D(−) and the L-form L(+). The anion (IV) of D-lactic acid is



$$\begin{array}{c} CO_2^- \\ \cdot \\ H.C.OH \\ \cdot \\ CH_3 \end{array} \qquad (IV)$$

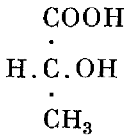
It is evident that the vertical dipole points upwards which implies that the solution of a salt with some strong base is *dextro* rotatory in agreement with results(11) arrived at in other ways. The D-lactic acid itself, however, is *laevo*rotatory(11).

This may have a rather natural explanation: like $-NH_2$ the group $-OH$ is basic although not so strongly as the former. A fraction of the acid in aquous solution may therefore be in the form (V)



$$\begin{array}{c} CO_2^- \\ \cdot \\ H.C.OH_2^+ \\ \cdot \\ CH_3 \end{array} \qquad (V)$$

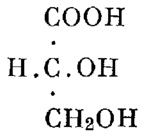
where the negative end of the horizontal dipole points to the left, which means that the substance is partially (−), while a molecule of the configuration (VI) must be (+).



$$\begin{array}{c} \mathrm{COOH} \\ \cdot \\ \mathrm{H.C.OH} \\ \cdot \\ \mathrm{CH_3} \end{array}$$

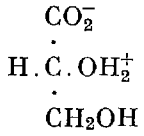
(VI)

D glyceric acid is known to be (−). In solution it is probably a mixture of (VII), (VIII), and (IX)



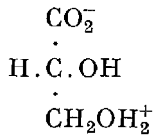
$$\begin{array}{c} \mathrm{COOH} \\ \cdot \\ \mathrm{H.C.OH} \\ \cdot \\ \mathrm{CH_2OH} \end{array}$$

(VII)



$$\begin{array}{c} \mathrm{CO_2^-} \\ \cdot \\ \mathrm{H.C.OH_2^+} \\ \cdot \\ \mathrm{CH_2OH} \end{array}$$

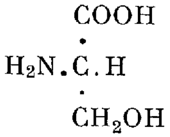
(VIII)



$$\begin{array}{c} \mathrm{CO_2^-} \\ \cdot \\ \mathrm{H.C.OH} \\ \cdot \\ \mathrm{CH_2OH_2^+} \end{array}$$

(IX)

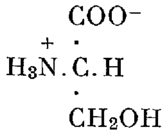
As the dipolemoment of $-\mathrm{COOH}$ is only about 1 D while that of $-\mathrm{CH_2OH}$ is about 1,7 D (VII) and (VIII) are both (−), but (IX) must be (+). Whether or not the sum of the contributions from the three forms (VII), (VIII) and (IX) will yield the result (−) known from other sources cannot be told without knowledge of the specific rotations of the forms and their distribution. In this case therefore no prediction of the sense of rotation of the substance in question can be made. It can be predicted, however, that the rotation should be (+) in a solution of a strong base, which agrees with the result from other sources.(13) L(−) Serine serves, like glyceraldehyde, as a standard from which the absolute configurations of other optically active compounds are being derived chemically (by substitutions which do not affect the active centre). Klyne states(14) that its configuration is intercorrelated chemically with that of D(+) glyceraldehyde (through a long series of reactions). On account of the $\mathrm{CH_2OH}$ group at the lower end of the three-carbon chain it is, however, not by far so easy to treat by means of the present method as alanine. To this comes another difficulty: One is apt to believe that the NH_2-group is analogous to the HO-group in so far that both dipoles H_2N-CH and HO-CH point to the left with their negative ends. According to the measurements of J. Estermann quoted by P. Debye in his book(7) this is, however, not so. He determined the dipolemoments of *o*, *m* and *p* amino-methylbenzoate and found that the *o*-compound had the smallest and the *p*-compound the greatest moment. This fact can hardly be interpreted otherwise than in the *p*-compound the two dipoles H_2N-C and C-$COOCH_3$ must point in the same direction with their negative ends. The dipoles H_2N-CH and HO-CH must therefore point in opposite directions. The same conclusions must be drawn from the fact that *p*-chloroaniline and *p*-nitro-aniline have dipolements much greater than that of aniline itself.(15) L-serine written in the conventional way is (X). As the vertical



$$\begin{array}{c} COOH \\ \cdot \\ H_2N.C.H \\ \cdot \\ CH_2OH \end{array}$$

(X)

dipole in this points downwards, (X) is actually (−), but, according to N. Bjerrum(9), a more probable configuration is

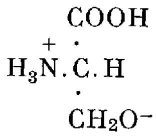


$$\begin{array}{c} COO^- \\ \overset{+}{}\ \cdot \\ H_3N.C.H \\ \cdot \\ CH_2OH \end{array}$$

(XI)

which, according to the present hypothesis should be (+), not (−).

There is however a third possibility namely:

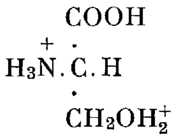


$$\begin{array}{c} COOH \\ \overset{+}{}\ \cdot \\ H_3N.C.H \\ \cdot \\ CH_2O^- \end{array}$$

(XII)

which is (−) .(XII) may seem to be a little too sophisticated. But, on the other hand, as CH_2OH according to the dipolemeasurements is more electronegative than COOH it cannot at all be excluded that the proton taken up by the

NH_2-group has migrated from the former rather than from the latter. But even so it is at the present state of affairs impossible to predict with any certainty the sense of the optical rotation of a mixture of the three forms of L-serine (X), (XI) and (XII). If, however, L-serine is dissolved in hydrochloric acid in stead of in water the rotation becomes (+), which agrees with (XIII):



$$\begin{array}{c} \mathrm{COOH} \\ \cdot \\ \overset{+}{\mathrm{H_3N}}.\mathrm{C}.\mathrm{H} \\ \cdot \\ \mathrm{CH_2OH_2^+} \end{array}$$

(XIII)

The whole question of the dependence of the rotatory power of L-serine as a function of the acidity of the solution should evidently be investigated experimentally before anything definite can be said on the question of agreement between the present hypothesis and the facts.

The results obtained in the preceding paragraphs seem sufficiently promising to justify an application of the same hypothesis to cases, where more than one carbon-atom comes into play. As will be seen from the foregoing pages there is no doubt that the hypothesis leads to the correct result when the configuration and the distribution of charges is unambiguous. In cases where a molecule containing two or more than two carbon-atoms bound in such a way to each other that the structure is rigid, the dipoles which are components of the screwlike quadrupole may be similar or identical. This latter extremely simple case may give rise to optical activity, which of course is impossible in the case of only one carbon-atom. Tartaric acid is the best known example of this kind of optical activity but the tartaric acid molecule is not rigid as the two carbon's can be twisted (although perhaps not quite freely) relatively to each other. Other important examples are XX vicinal disubstitutes of cyclohexane.

Configuration and Rotatory Power of Vicinal XX-substituted Cyclohexane

One of the most convenient ways of illustrating the structure of cyclohexane in the Sachse chair form and its derivatives is the socalled Newman-projection, in which two pairs of C-atoms are in the same plane while one C is above and the opposite one is below that plane. As cyclohexane deriva-

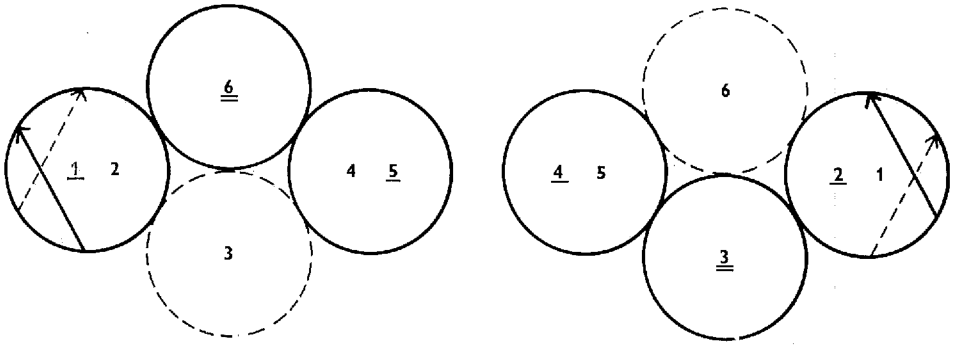


Fig. 1 shows a Newman-projection of 1,2 *cis*-cyclohexane XX where X is some eletronegative group. The arrows point to the negative ends of the dipoles. When drawn with heavy lines they are meant to be before the plane of the paper, when drawn broken they are behind the same plane. The same is true of the two circles which represent C_6 and C_3. The numerals in the circles denote the numbers of the six C-atoms. Numerals which relate to the foremost C-atoms are doubly underlined, those in the next plane are underlined with a single line and those behind the plane of the paper are not underlined. The diagram to the left is intended to show the molecule seen in the direction from C_6 to C_3, that to the right shows the same molecule seen in exactly the opposite direction. It is seen that the forces in the pair which tends to twist the electric field-vector of photons which impinges on an ensemble of molecules of the kind considered have the same direction throughout the molecule and that furthermore the contribution to the twist from the two situations illustrated in fig. 1 must be exactly equal because the two situations are equally probable. It is evident that the quadrupole has the character of a d-screw and that therefore the substance must have (—) rotation. If both dipoles are inverted the optical rotation remains unchanged in direction.

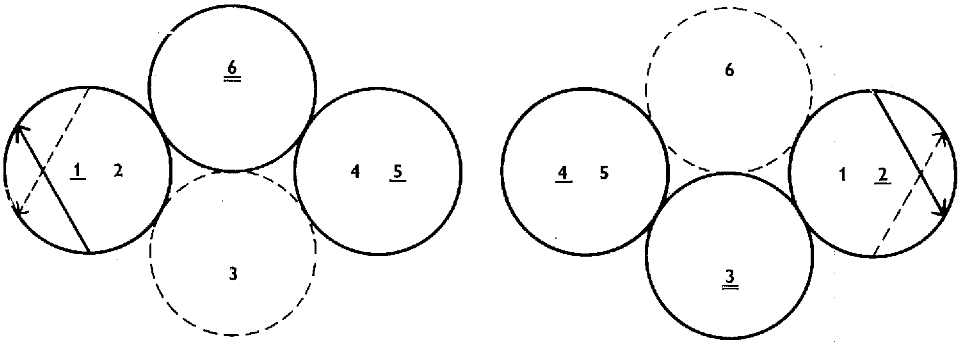


Fig. 2 shows a Newman-projection of a 1,2 cyclohexane XX molecule in *trans*(ee) configuration. The conventions from fig. 1 regarding positions relative to the plane of the paper and the meanings of the left and the right diagrams apply also here. Here again a photon has ecaxtly the same probality of meeting a molecule in the situation "left" and in the situation "right" when it impinges on an ensemble of molecules of the kind considered. But from this follows that the forces in the pairs which should tend to twist the electric vectors to the left compensate each other exactly throught the molecule so that the rotation becomes zero.

The same is evidently true, if both arrows are inverted, in which case the diagram would represent the *trans*(aa) configuration.

tives are stereochemically related to carbohydrates in pyranose-form, it is convenient to number the C-atoms similarly as it is done by convention in the pyranose sugars, C_6 corresponding to O_5 in the sugars while the carbons 1, 2, 4, and 5 are in one plane and C_6 above and C_3 below that plane.

Fig. 1 and fig. 2 are intended to illustrate the situation. A polarized electromagnetic wawe-front or a bundle of polarized photons advancing in parallel, like the rows in a marching army, must meet molecules in the two kinds of orientation relative to the direction of propagation of the front, pictured respectively to the left and to the right, exactly equally often. In the case of fig. 1, the *cis*(ea), the field vectors of the photons will be exposed to shearing forces from "left" and "right" molecules which are pairwise equal and have pairwise the same direction. During the advancement of the front through the molecule the direction of the forces will perform a screwlike pattern which in this case corresponds to the pattern of a *d*-screw. Consequently the electric photon vectors will be exposed to a twist to the right during the passage of the front through the molecule.

In fig. 2, the *trans*-(ee) case, the situation is quite different, Also here the wavefront must pass corresponding planes in pairs of "left" and "right" molecules exactly equally often, and the forces to which the photon-vectors are exposed are equal in magnitude for the "left" and "right" molecules in the pair, but, their directions are opposite to each other in corresponding planes throughout the molequles. Consecuently the twisting forces will add up to zero and there will be no twist of the electrical vector of the photons and therefore no rotation of the plane of polarization.

If, in fig. 2, the arrows are inverted, fig. 2 visualizes a *trans*(aa) compound and it is seen that also this compound must be optically inactive. It follows that that isomer, which can be separated into optical antipodes must be the *cis*-form, and that (or those) which cannot must be *trans*-forms.

This result agrees with that arrived at in a group of papers(16) published in these communications, but it disagrees with the current assumption that the optically inactive form like the *meso*-tartaric acid is a *cis*-form.

It should be added, that if the two dipoles in the quadrupole corresponding to figures 1 and 2 are different, one must expect the rotation of the *trans*-form to be less than that of the *cis*-form, but not zero.

This allows a very natural interpretation of the finding of VAVON and PEIGNIER(17) quoted by ELIEL in his well known book18): A vicinal hexahydrophtalic acid, which is quoted by ELIEL as being *cis* but which the writer for several reasons believes to be *trans*(ee) has been prepared by saponification under mild conditions from its monomethylester which was optically active while the acid itself became optically inactive. As will be seen, this behaviour is exactly what one should expect from the *trans*-acid if the writers arguments are correct.

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