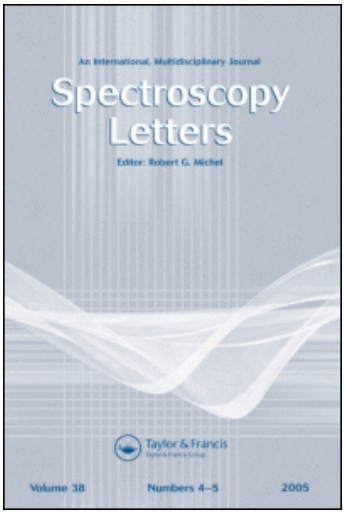

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Linear Dichroism of Aromatic Molecules in Stretched Polyethylene

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LINEAR DICHROISM OF AROMATIC MOLECULES IN STRETCHED POLYETHYLENE

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Abstract

The form of the distribution function of a solute in uniaxially stretched polyethylene is discussed. Conditions and formulas are given for the determination of independent (reduced) absorption spectra of chromophores with absorption polarized in three mutually perpendicular directions, and an experimental result is presented. The "orientation triangle" is defined, and its usefulness in studies of linear dichroism is emphasized.

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INTRODUCTION

The orientation distribution function $\rho(\alpha,\beta,\gamma)$ of solute molecules in a stretched polymer can be expanded in the complete set of rotation matrices $D^{(j)}_{mm'}(\alpha,\beta,\gamma)$:

$$\rho(\alpha,\beta,\gamma) = \frac{1}{8\pi^2} \sum_{j,m,m'} \rho(j,m,m') D^{(j)}_{mm'}(\alpha,\beta,\gamma),$$

where α, β, and γ are the Euler angles describing the orientation of a molecule-fixed coordinate system with respect to the polymer-fixed coordinate system. In a uniaxially stretched polymer, many of the coefficients $\rho(j,m,m')$ vanish and others are related by symmetry, but generally an infinite number of independent coefficients still are non-zero. Experiments provide quantities such as

$$\langle\cos^2\beta\rangle = 1/3 + (2/15)\rho(200),$$

$$\langle\cos^2\beta'\rangle = 1/3 + (1/5\sqrt{6})\left[\rho(202) + \rho(20\text{-}2)\right] - (1/15)\rho(200),$$

$$\langle\cos^4\beta\rangle = 1/5 + (4/35)\rho(200) + (8/315)\rho(400),$$

$$\langle\cos^2\beta.\cos^2\beta'\rangle = 1/15 + (1/35\sqrt{6})\left[\rho(202) + \rho(20\text{-}2)\right] + (1/105)\rho(200) + (1/63)(\sqrt{2/5})\left[\rho(402) + \rho(40\text{-}2)\right] - (4/315)\rho(400),$$

$$\langle\cos^4\beta'\rangle = 1/5 + (\sqrt{6}/35)\left[\rho(202) + \rho(20\text{-}2)\right] - (2/35)\rho(200) + (3/315)\rho(400) - (1/63)(\sqrt{2/5})\left[\rho(402) + \rho(40\text{-}2)\right] + (1/9\sqrt{70})\left[\rho(404) + \rho(40\text{-}4)\right],$$

where β and β' are the angles between the molecular "long" (z) and "medium" (y) axis and the polymer stretching direction ($\cos^2\beta' = \sin^2\beta\cos^2\gamma$). The "short" (x) axis forms an angle β'' with the stretching direction ($\langle\cos^2\beta\rangle+\langle\cos^2\beta'\rangle+\langle\cos^2\beta''\rangle = 1$). Measurement of linear dichroism of a trans-

sition polarized along x,y,z yields $\langle\cos^2\beta\rangle$, $\langle\cos^2\beta'\rangle$, $\langle\cos^2\beta''\rangle$, respectively (e.g., $\langle\cos^2\beta\rangle = E^z_{\parallel}/(2E^z_{\perp} + E^z_{\parallel})$, where $E^z_{\parallel}$ and $E^z_{\perp}$ are the parallel and perpendicular experimental dichroic intensities of a z-polarized transition). Similarly, quantities of type $\langle\cos^4\beta\rangle$ can be related to the degree of polarization of solute fluorescence or Raman spectra. Even when results of several methods are combined, usually only a very small number of the independent coefficients $\rho(j,m,m')$ can be derived. Therefore, it is in general impossible to deduce unambiguously the function $\rho(\alpha,\beta,\gamma)$, but, on the other hand, some functional forms can be excluded on the basis of such data, as we shall see in the following.

LINEAR DICHROISM OF A "THREE-DIMENSIONAL CHROMOPHORE"

For the moment, we shall consider solutes of sufficiently high symmetry (C_{2v}, D_{2h}) in which possible z, y, and x directions are given by symmetry. If the two "longest" dimensions of the solute have equal orienting ability, either one can be labelled z, the other is y (two perpendicular in-plane axes of coronene). If the two shortest dimensions have equal orienting ability, either one can be called x, the other is y (two perpendicular short axes in 2-butyne). We use "long", "short", etc., in quotation marks since factors other than shape alone may influence the orienting ability. With the notation $K_1 = \langle\cos^2\beta\rangle$, $K_2 = \langle\cos^2\beta'\rangle$,

$$E_{\parallel} = K_1.A_z + K_2.A_y + (1-K_1-K_2)A_x,$$

$$E_{\perp} = (1-K_1).A_z/2 + (1-K_2)A_y/2 + (K_1+K_2)A_x/2,$$

where A_z, A_y, and A_x are the components of absorption polarized along the z, y, and x directions, respectively. Using the usual reduction procedure, we find numbers d_z, d_y, and d_x such that z-polarized, y-polarized, and x-

polarized spectral features just disappear from the linear combinations $(E_{\parallel} - d_z E_{\perp})$, $(E_{\parallel} - d_y E_{\perp})$, and $(E_{\parallel} - d_x E_{\perp})$.

Then,

$$K_1 = d_z/(2+d_z),\ K_2 = d_y/(2+d_y) = 2/(2+d_x) - d_z/(2+d_z),$$

$$E_{\parallel} - d_z E_{\perp} = \left[(K_1-K_2)A_y + (2K_1+K_2-1)A_x\right]/(K_1-1),$$

$$E_{\parallel} - d_y E_{\perp} = \left[(K_1-K_2)A_z - (2K_2+K_1-1)A_x\right]/(1-K_2),$$

$$E_{\parallel} - d_x E_{\perp} = \left[(2K_1+K_2-1)A_z + (2K_2+K_1-1)A_y\right]/(K_1+K_2).$$

This evaluation procedure puts all three principal directions on equal footing; it is necessary to recognize z, y, and x-polarized spectral features. This is quite straightforward if more than one feature (peak, shoulder) is present in each polarization, since all features of equal polarization disappear simultaneously in the trial-and-error reduction search. If only one feature of a particular polarization (x,y,z) is present, determination of the corresponding d value will require the assumption that a spectral feature of identical shape and location is not present in either of the other two components of polarized absorption. If no spectral feature polarized in a particular direction can be recognized, the corresponding d value cannot be determined.

From the definitions of the axes, $d_z \geq d_y \geq d_x$, and thus, $K_1 \geq K_2$, $K_2 \geq (1-K_1)/2$. From the properties of direction cosines, $K_1 + K_2 \leq 1$, and therefore, all points (K_1,K_2) must lie inside the "orientation triangle" shown in Fig. 1. With other definitions of labels for the axes, points (K_1,K_2) may lie outside the triangle.

The relation between d_z, d_y, and d_x is

$$2/(2+d_x) = d_y/(2+d_y) + d_z/(2+d_z) = K_1 + K_2 ,$$

and this, in principle, permits a recognition of, say, x-polarized features in the spectrum once z- and y-polarized features have been recognized. The fulfillment of the relation can be used as a test of the accuracy of the reduction procedure.

It is clear that in general it is impossible to find the independent absorption curves A_z, A_y, and A_x from a single measurement of $E_{||}$ and $E_{\perp}$. Some special cases deserve mention. If the orienting properties of the z and y dimensions are equal (disc-shaped molecules, $d_z = d_y = d$), $K_1 = K_2 = K$, and it is possible to obtain $A_z + A_y$ and A_x separately:

$$A_z + A_y = (E_{||} - d_x E_{\perp})d/(d-1),$$

$$A_x = (E_{||} - dE_{\perp})/(1-d).$$

If the orienting properties of the y and x dimensions are equal (rod-shaped molecules, $d_y = d_x = d$), $K_2 = (1-K_1)/2$, and it is possible to obtain A_z and $A_y + A_x$ separately:

$$A_z = (E_{||} - dE_{\perp})(d_z+1)/(d_z-1),$$

$$A_y + A_x = 2(E_{||} - d_z E_{\perp})/(1-d_z).$$

If the orienting properties of all three dimensions are equal, no dichroism will be observed ($E_{||} = E_{\perp}$), and reduction is impossible. If a spectral region can be found in which A_z, A_y, or A_x vanishes, the other two components can be determined. For instance, in the spectral region in which out-of-plane polarized intensity is negligible in aromatic molecules ($A_x = 0$),

$$A_z = (E_{||} - d_y E_{\perp})(2+d_z)/(d_z-d_y),$$

$$A_y = (E_{||} - d_z E_{\perp})(2+d_y)/(d_y-d_z).$$

In principle, it is possible to find the independent absorption curves A_z, A_y, and A_x even in the general case from two measurements of $E_{||}$ and $E_{\perp}$ on two differently oriented samples, one characterized by factors K_1 and K_2, the other by K_1' and K_2' (e.g., in two polymer samples stretched to a different degree). This is only possible if the measurement yields at least three linearly independent curves E. It is easily seen that this will be the case if

$$(3K_2-1)(3K_1'-1) \neq (3K_1-1)(3K_2'-1),$$

i.e., if the straight line going through points (K_1,K_2) and (K_1',K_2') does not pass through the point (1/3, 1/3). If this relation is nearly fulfilled, the determination will be very inaccurate.

THE "ORIENTATION TRIANGLE"

Reduction factors d were measured for $\pi\pi^*$ transitions in a series of symmetrical aromatic compounds oriented in stretched polyethylene (~500%). Consideration of the values of d/(2+d) showed that the two in-plane directions correspond to the z and y axes and the out-of-plane direction to the x axis as defined above ($d_z \geq d_y \geq d_x$). The values of K_2 and K_1 resulting from these experiments are plotted against each other in Fig. 1. As expected, the points lie inside the "orientation triangle". The accuracy of the points shown is limited by the accuracy of the reduction procedure, which is roughly indicated by the size of the points, and by the accuracy of the assumption that certain spectral features are due to purely polarized absorption. In many cases, this assumption has been checked against absolute measurements on single crystals and was found to be correct to an excellent degree. Thus, there is no doubt that the points in Fig. 1 are indeed as scattered over the inside of the triangle shown as they appear to be. Comparison with absolute measurements also showed that the z axis corresponds invariably to the longest in-plane

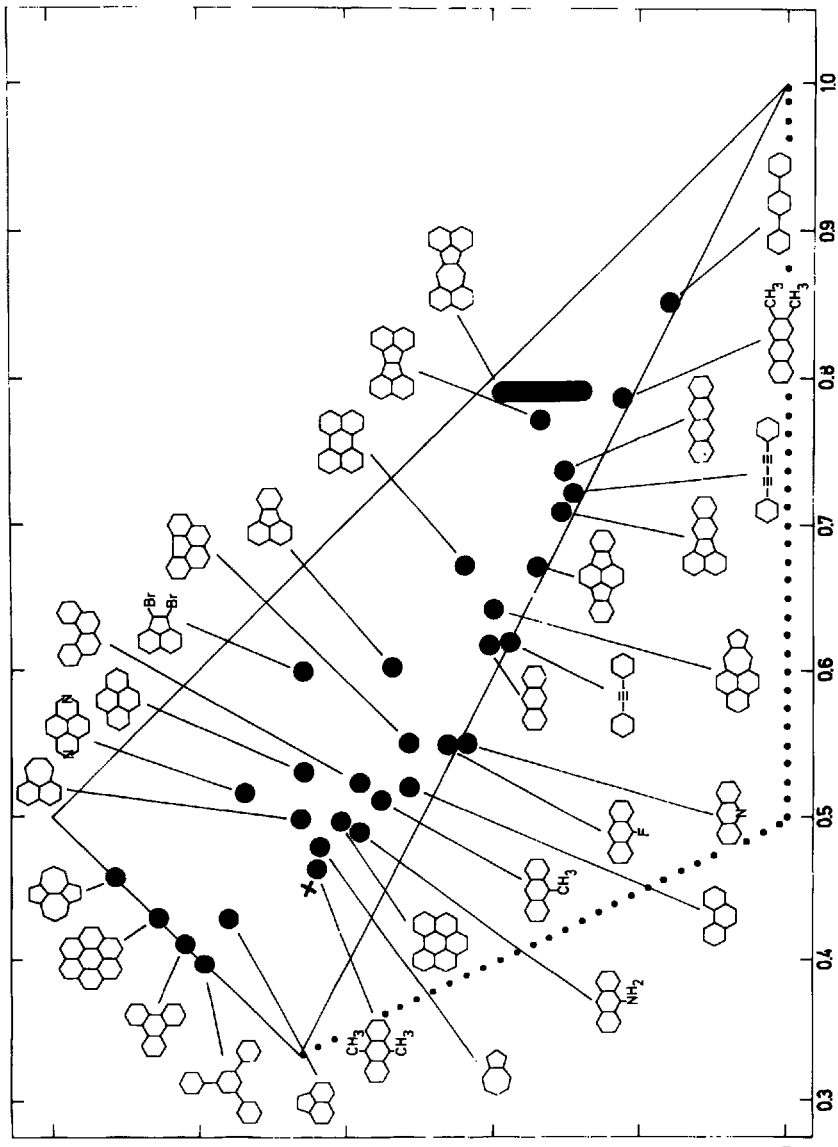


Fig. 1 Orientation factors K_1 and K_2. The value of K_2 for dinaphthazulene is rather uncertain because short-axis polarized spectral features are poorly developed in its spectrum.

dimension of the aromatic molecule and that the y axis corresponds to its short in-plane dimension, and this then allows the stretched sheet method to be used for absolute polarization determinations, at least for molecules of the general type considered here.

Each orientation distribution function $\rho(\alpha,\beta,\gamma)$ corresponds to a point in Fig. 1. From the equations given at the outset it is clear that K_1 and K_2, and thus the location of the corresponding point, are fully determined by $\rho(200)$ and $[\rho(202) + \rho(20\text{-}2)]$ alone, i.e., all distribution functions which share these particular values of $\rho(j,m,m')$ correspond to the same point in the graph. Any distribution function $\rho(\alpha,\beta,\gamma)$ can be mapped into Fig. 1, but in general, an inverse mapping is impossible. This illustration of the fact that $\rho(\alpha,\beta,\gamma)$ cannot be derived from a finite number of quantities such as $\langle\cos^2\beta\rangle$ and $\langle\cos^4\beta\rangle$ perhaps would not need to be mentioned, but confusion on this point occasionally occurs in the literature where attempts are made to prove that $\rho(\alpha,\beta,\gamma)$ has some particular form (e.g., part of the molecules randomly oriented and part perfectly aligned). Clearly, all one can do on the basis of these measurements alone is to prove that $\rho(\alpha,\beta,\gamma)$ does not have some particular form, and an example is given below.

Three important limiting forms of orientation distribution correspond to the vertices of the triangle shown in full lines in Fig. 1: isotropic distribution ($K_1 = K_2 = 1/3$), perfect alignment of molecular z axis with the stretching direction ($K_1 = 1$, $K_2 = 0$), and perfect alignment of the molecular zy plane with the stretching direction, with perfect equivalence of the z and y axes ($K_1 = K_2 = 1/2$). Three more general limiting forms of orientation distribution correspond to the sides of the triangle: distributions in which z and y are equivalent (disc-like orientation) correspond to the line $K_2 = K_1$, those in which y and x are equivalent (rod-like orientation) correspond to the line $K_2 = (1\text{-}K_1)/2$, and those in which the molecular zy plane is perfectly

aligned with the stretching direction, but the z and y axes are not necessarily equivalent, correspond to the line $K_2 = 1-K_1$. Points inside the triangle correspond to more general types of orientation distribution for which the molecular zy plane tends to orient along the stretching direction rather than perpendicular to it (the Euler angle γ prefers values near 0^o or 180^o to those near 90^o). It is seen that all experimental points correspond to distributions of this type or, in a few instances, to either rod-like or disc-like behavior.

The fact that many of the observed points lie above the "line of rod-like orientations" $K_2 = (1-K_1)/2$ rather than on it shows that the zy plane rather than the z axis alone tends to align with the stretching direction. Therefore, it is not correct to limit one's attention to those functions $\rho(\alpha,\beta,\gamma)$ for which angle γ is distributed uniformly, i.e., in which the two shorter axes y and x are equivalent. An example of such a distribution is one in which a part of the molecules is oriented perfectly and another part randomly. This and other types of "uniform γ" distributions are frequently assumed in the literature in spite of previous criticism and evidence to the contrary[1], presumably since they simplify the evaluation of the results. Fig. 1 makes it abundantly clear that uniform γ distribution can only be assumed for some molecules, but not in general. It may be noted in passing that the relation of d_x to d_z and d_y acquires a particularly clear form when $\langle\cos^2\beta''\rangle$ is plotted in Fig. 1 against K_1: the point $(\langle\cos^2\beta''\rangle, K_1)$ lies as much below the "line of rod-like orientation" $\left[K_2 = (1-K_1)/2\right]$ as the point (K_2,K_1) lies above it. As the point (K_2,K_1) is allowed to roam throughout the triangle shown in full lines, the counterpart point $(\langle\cos^2\beta''\rangle, K_1)$ roams through the dotted triangle below it.

The location of the points inside the triangle in Fig. 1 is clearly related to molecular shape. Points for disc-shaped molecules lie on the line $K_2 = K_1$, and tend to be farther away from the point of random orientation

($K_1 = K_2 = 1/3$) as the molecular size increases. Approximately rod-shaped molecules yield points near the line $K_2 = (1-K_1)/2$, farther away from the point of random orientation as their length increases. Points for other molecules lie inside the triangle and form an almost continuous transition between the two limiting types of orientation. The distance of the points from the line of rod-like orientations $K_2 = (1-K_1)/2$ increases as the difference of the molecular y and x dimensions increases, and the distance from the line of disc-like orientations $K_2 = K_1$ increases as the difference of the z and y dimensions increases.

However, shape clearly is not the only factor which determines the location of points K_1 and K_2, and perhaps not the primary factor at all, since it may reflect some other molecular properties such as polarizability and its anisotropy. An indication that shape alone is not sufficient for accurate predictions is given by the comparison of points for anthracene and phenazine. Still, a fairly reasonable if not completely accurate prediction of K_1 and K_2 for a new molecule appears possible by comparison with values for related molecules of similar shape. This is useful for the determination of polarization directions in molecules of lower symmetry[1] in which it is not possible to assume that transitions lie along the orientation axis or in one of two directions perpendicular to it. In particular, for $\pi\pi^*$ transitions knowledge of K_1, K_2, and measured linear dichroism permits a determination of the angles between the polarization directions and the molecular orientation axis. The remaining problem then is to relate the direction of the orientation axis to the molecular framework. Inspection of Fig. 1 indicates that a reasonable first approximation is obtained by taking this direction to be that along which the molecule exposes its smallest cross-section, but better estimates may become possible in the future.

This preliminary report presents data for only a limited number of aromatic molecules and, moreover, some of the points were obtained from measurements at room temperature, others from measurements at low temperature. In a

full publication, we are planning to study additional molecules, and to compare only data obtained under similar conditions. This will hopefully facilitate the prediction of K_1 and K_2 values for new molecules.

EXPERIMENTAL RESULTS FOR A "THREE-DIMENSIONAL CHROMOPHORE"

The X-ray structure analysis[2] of 6b,10b-dihydrobenzo [j]cyclobut[a]-acenaphthylene I shows that it has C_s symmetry and that the dihedral angle formed by the plane of the benzocyclobutene ring and the plane of the acenaphthene ring is 115°. The absorption spectrum of I resembles closely the sum of the absorption spectra of these two chromophores. In stretched polyethylene, the long axis of the naphthalene moiety (z) aligns with the stretching direction: the reduction factor of the L_b and B_b bands of naphthalene, clearly apparent in the spectra, is $d_z = 1.67$. The reduction factor of the L_a band of naphthalene, polarized along y in formula I, is $d_y = 0.95$. The location of the corresponding point in the "orientation triangle" is shown by a cross in Fig. 1. The last spectral feature to disappear in the reduction procedure is the benzene L_b band, polarized along a line $\underline{v}$ contained in the benzene ring and crossing bonds, i.e. the line in which the benzene ring is cut by the yx plane in formula I, $d_v = 0.55$. The reduced absorption curves clearly show that the three types of polarization require three different values of d (Fig. 2). Already the fact that the L_b band of benzene and the L_a band of naphthalene, which are both polarized perpendicular to the z axis of formula I, require considerably different reduction factors proves that all directions perpendicular to z are not equivalent, i.e. that once again, the distribution of the Euler angle γ is not uniform. To see whether the three observed reduction factors, d_z, d_y, and d_v, are mutually compatible, one needs to modify slightly the formulas derived above, since d_x is not directly accessible. When account is taken of the contributions provided by absorption polarized along $v(A_v)$ both to $A_y(A_v.\sin^2\alpha)$ and to $A_x(A_v.\cos^2\alpha)$, $\alpha = 25°$, one obtains the relation $d_v = 2\left[(1-K_1)\cos^2\alpha + K_2(1-2\cos^2\alpha)\right] / \left[1-(1-K_1)\cos^2\alpha - K_2(1-2\cos^2\alpha)\right]$, which gives a numerical value of $d_v = 0.55$

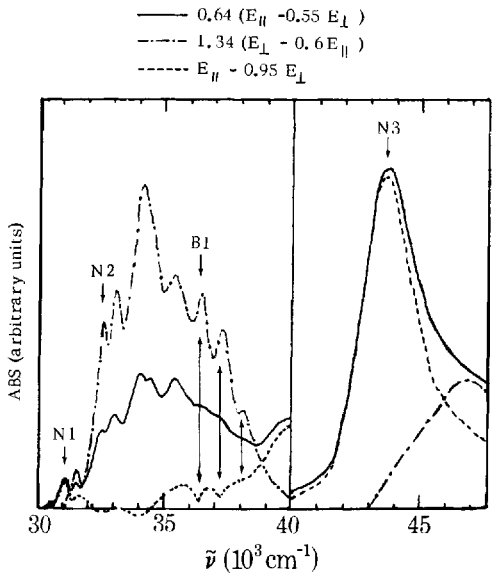
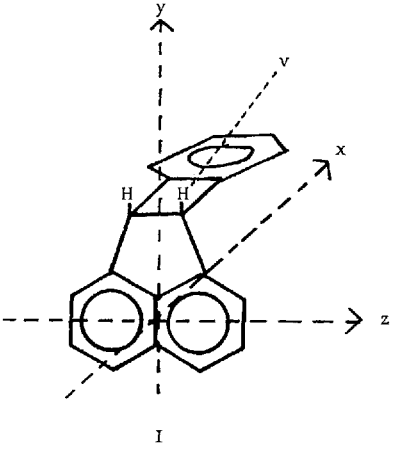


Fig. 2 Reduced spectra of I (polyethylene), showing absorption bands of the naphthalene (N) and benzene (B) subunits.

using $d_z = 1.67$ and $d_y = 0.95$ in agreement with the measured value of d_v. Thus, the measurements on I not only provide a very clear-cut example of a non-uniform γ distribution, but also provide an internal consistency check for the formulation proposed here for "three-dimensional chromophores".



I

CONCLUSIONS

The conclusions reached here can be summarized as follows:

a. Although it is not possible to derive the form of the distribution function of a solute in uniaxially stretched polyethylene unambiguously from the measurement of a finite number of dichroic factors such as $\langle\cos^2\beta\rangle$, $\langle\cos^4\beta\rangle$, etc., such measurement can show that some forms of the orientation distribution function, and thus some models for orientation, are inappropriate. This statement is trivial but does not seem to be always appreciated in studies of linear dichroism.

b. Theory for linear dichroism of chromophores with absorptions polarized in three mutually perpendicular directions is presented and conditions under which the independent absorption spectra can be determined are stated. Extension to more general cases of "three-dimensional chromophores" is straightforward and experimental results for one such well-defined example are given, illustrating the internal consistency of the theory.

c. The "orientation triangle", resulting from a plot of $\langle\cos^2\beta'\rangle$ against $\langle\cos^2\beta\rangle$, is shown to represent a convenient framework for discussions of those aspects of solute orientation distribution functions which play a role in studies of linear dichroism. It is already fairly densely populated with points for symmetrical aromatic molecules. As their number increases further, predictions of orientation factors will become even easier. Already now, fairly adequate predictions are possible, permitting determination of polarization directions in aromatic molecules of low symmetry.

d. Two independent lines of evidence make it crystal clear that for numerous but not all aromatic solutes the distribution of the Euler angle γ, which describes rotation of the molecule along its own long axis, is not uniform, i.e., the two short axes y and x are not equivalent and the solutes do not behave like rods.

The deviation from rod-like behavior is due to the tendency of the molecular plane zy to align with the stretching direction.

This conclusion needs to be emphasized although it has already been reached some time ago[1] on the basis of fewer experimental data, since the assumption of equivalence of x and y, i.e., of uniform γ distribution, keeps reappearing even in the recent literature.

Finally, it should be emphasized that much of the material presented in this survey is not original. The theory of rotation matrices is available in books[3]. Expressions for linear dichroism in the special case of rod-like molecules have been formulated by numerous authors[4], and also expressions for the special case of disc-like molecules have been published[5]. The reduction procedure and its applications to aromatic molecules with negligible out-of-plane absorption are well known[1]. The general equations for a "three-dimensional chromophore" have been very briefly mentioned recently[6]. A brief description of the "orientation triangle" and references to the origin of some of the experimental points in it have also appeared recently[7]. A different but essentially equivalent form of the "orientation triangle" was discussed in ref. 8. Leading references to numerous individual cases in which the assumption of uniform γ distribution has been found untenable can be found in ref. 7.

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