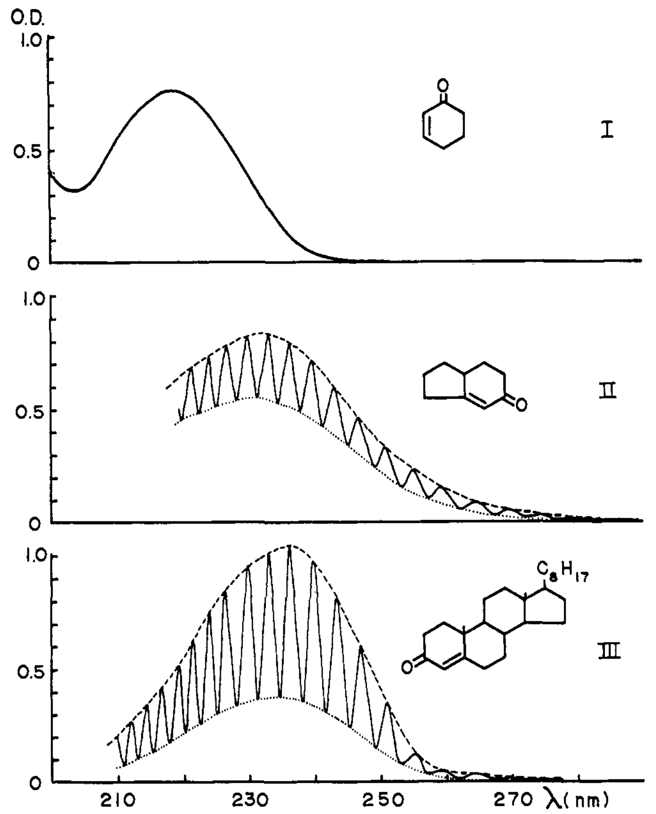

Figure 3. The linear dichroic curve of I, II, and III measured with CD-HC accessory:[10] (- - -) the curve of the interpolated optical densities obtained by light polarized in the direction of stretching; (· · ·) the curve obtained by light polarized perpendicular to the direction of stretching.

clear that the dichroic ratio as a function of β is a molecular property, which is specific to the structure of the incorporated material. Furthermore since every ellipse has an axis in the direction of stretching, regardless of the molecular skeleton, the chromophore involved, or its position in the skeleton, this direction must be an axis of symmetry of the assembly of the oriented incorporated molecules. For such an orientation, the dichroic ratio is expressed by eq 1.[5] α represents the angle between the transition moment vec-

$$\mathbf{d}_0 = \frac{f\cos^2\alpha + {}^1/_3(1-f)}{{}^1/_2 f\sin^2\alpha + {}^1/_3(1-f)} \quad (\beta = 0°) \tag{1}$$

tor of the chromophore and the longitudinal axis of the molecule and f is a factor which depends on the orientation distribution.

The equivalent dichroism will be obtained by a film where a fraction f is completely oriented along the axis of symmetry and a fraction $1 - f$ is completely randomized.

We have found that the same dichroism is obtained whether the compound is incorporated prior to or after orientation of the film (when done under identical conditions). Hence the orientation of the incorporated compound merely reflects the orientation of the polymer. On the other hand we found a strong dependence of the dichroism on the skeletal geometrical isotropy, *i.e.*, compound I shows no dichroism, compound II shows only slight dichroism, and compound III shows a very strong dichroism (Figure 3).[6]

Since polyethylene is known to be composed of crystallites and an amorphous fraction, the term f of the equation might represent the partition of the incorporated material between the amorphous and crystalline fractions. As polar interactions between polyethylene and the incorporated material are small, f will be common to all molecules having the same geometrical skeleton. α represents a molecular property and will be different from one molecule to another. Measuring a few such selected compounds, the equation can be solved, and the values of f and the various α can be deduced as can the direction of the transition moment vector of the chromophore and the longitudinal axis of the molecule.

Application of the method to specific chromophores and to some structural as well as conformational problems will be discussed in forthcoming publications.

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one direction, when further stretched in that direction the yield point will be reached immediately. *Cf.* T. O. J. Kresser, "Reinhold Plastics Application Series I. Polyethylene," Reinhold Publishing Corp., New York, N. Y., 1957, p 55. However a dependence of the dichroic ratio on the degree of stretching is claimed by Tanizaki[11] for compounds incorporated in polyvinyl alcohol films. The analysis of this dependence is used by him for a quantitative interpretation of his results.

(5) The geometrical conditions for the validity of this equation were discussed by M. Beer, *Proc. Roy. Soc.* (London), **A236**, 136 (1956); *cf.* ref 1e and 1f.

(6) The transition measured is the π–π^* band of the α,β-unsaturated carbonyl chromophores.

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Studies in Linear Dichroism. II.[1] Measurement of the Transition Moment Vector of α,β-Unsaturated Ketones, and of Some Geometrical Properties of Steroids

Sir:

In a preceding publication[1] we have discussed the use of eq 1 for the measurements of the dichroic ratio of molecules incorporated in stretched polyethylene films.

$$\mathbf{d}_0 = \frac{f\cos^2\alpha + {}^1/_3(1-f)}{{}^1/_2 f\sin^2\alpha + {}^1/_3(1-f)} \tag{1}$$

where f is the distribution factor of the incorporated molecules in the oriented film and α represents the angle between the longitudinal axis and the transition moment vector of the chromophores.

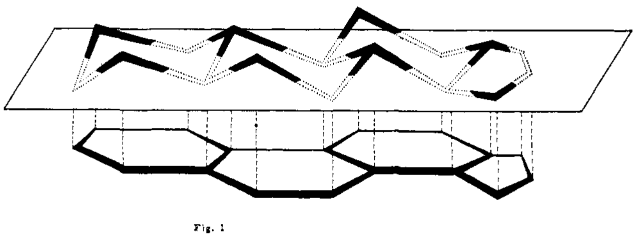

Figure 1. Projection of a steroid molecule on a dissecting plane.

When the measurements of dichroic ratios ($\mathbf{d}_0$) are applied to chromophores within molecules possessing

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(1) For part I, see A. Yogev, L. Margulies, D. Amar, and Y. Mazur, *J. Am. Chem. Soc.*, **91**, 4558 (1969).

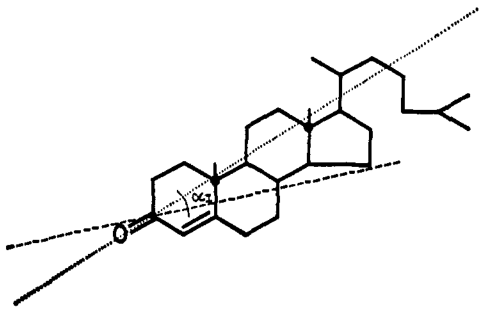

Figure 2. Measurement of α_I, the angle between (·········) the longitudinal axis and (- - - - - -) the π–π* transition moment vector of Δ^4-cholesten-3-one (I).

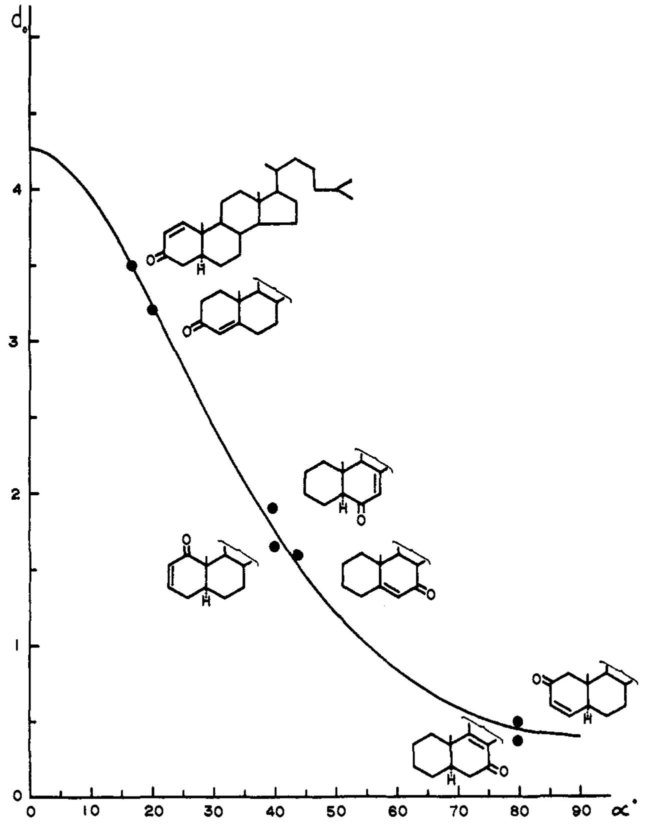

Figure 3. Plot of the dichroic ratio $\mathbf{d}_0$ *vs.* α according to eq 1 for the distribution factor $f = 0.5$. The circles are measured d_0 values of cholestenones plotted *vs.* α values calculated from a geometrical model.

the same carbon skeleton the f values may be assumed to be very nearly the same regardless of the type of chromophores considered or its position within the carbon framework. The measured $\mathbf{d}_0$ values of any two such compounds together with the use of the geometrical relationship between the two respective chromophores leads to the solution of (1).

We have measured the dichroic ratios of some steroidal α,β-unsaturated ketones[2] and applied the above-mentioned considerations to establish both the f and α values for those compounds.

In the normal steroidal skeleton, where all the rings are *trans* fused, the centers of all C–C ring bonds lie very nearly in a common plane. The projection of the molecule on this plane has the shape shown in Figure 1, where all ring angles are 120°. In α,β-unsaturated steroidal ketones, the plane defined by the three trigonal carbon atoms can be said to be very nearly identical with the above plane. Bearing such facts in mind, the sum of α_I and α_{II} in Δ^4-cholesten-3-one (I) and Δ^2-cholesten-1-one (II), respectively, seems to be independent of the virtual direction of the transition moment vector or the longitudinal axis of the molecule, as long as they are chosen in the same way in both cases.[3] Since from model considerations the sum of α values for I and II equals 60° and their $\mathbf{d}_0$ values were found to be 3.2 and 1.65,[4] eq 1 may be solved for both compounds, giving $f = 0.5$, $\alpha_I = 20°$, and $\alpha_{II} = 40°$. Similarly the f value for androstane derivatives using the values obtained from analogous compounds was found to be 0.3.

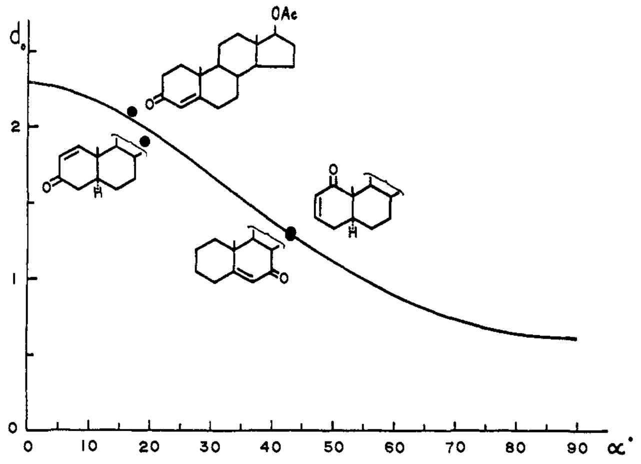

Figure 4. Plot of the dichroic ratio d_0 *vs.* α according to eq 1 for the distribution factor $f = 0.3$. The circles are measured d_0 values of 17β-acetoxyandrostenones plotted *vs.* α values calculated from a geometrical model.

Since f values for the two series of ketones was already established, any single measurement of $\mathbf{d}_0$ for any additional compound in each series and substitution in eq 1 will give their α values. Thus for Δ^1-3-ketones in the cholestane and androstane series the found $\mathbf{d}_0$ and the calculated α values were: 3.5, 1.9 and 14°, 21°, respectively.

Geometrical correlation of these latter α values with those obtained for either I or II gives both the transition moment vector and the direction of the longitudinal axis in the stretched film, as shown in Figure 2. The $\mathbf{d}_0$ values obtained for a number of the ketones are plotted in Figures 3 and 4 against the α values calculated from the geometrical model. The plots of α *vs.* $\mathbf{d}_0$ for $f = 0.5$ and 0.3 (cholestane and androstane series, respectively) are also given in the same figures. It is apparent from these figures that in most cases the linear dichroism is very sensitive to α; hence a very accurate

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[2] The transition measured is the π–π* band which is assumed to be polarized in the plane of the molecule.

[3] This can be shown by arbitrarily choosing directions for the transition moment vector and the longitudinal axis of the molecules, then varying one of them by a value γ. By this operation α_I becomes $\alpha_I + \gamma$ and α_{II} becomes $\alpha_{II} - \gamma$, and the sum remains constant.

[4] Three miligrams of each compound was dissolved in a few drops of cyclohexane or chloroform, in a narrow glass tube. A glass rod was immersed in the solution to diminish the free volume, and a 5 × 2.5 × 0.01 mm film was put between the glass rod and the tube walls. The temperature was kept 60° for 24 hr, the film was washed, dried, and stretched, and the linear dichroism was measured. *Cf.* R. Eckert and H. Kuhn, *Z. Elektrochem.*, **64**, 356 (1960).

measurement of longitudinal axis or transition moment vector becomes possible.[5]

One important application emerging from our linear dichroism measurements is the possibility of distinguishing between *cis* and *trans* ring fusion in polycyclic ketones. This may be examplified in 17β-acetoxy-5β-Δ^2-androsten-1-one in which the angle between its transition moment and the longitudinal axis of the molecule exceeds 50°. The $\mathbf{d}_0$ found for this compound was <1 (0.8), in accord with our expectations.

(5) Since the direction of the transition moment is obtained from an absorption phenomenon measurement, which depends on a squared value, it is only possible to define the axis along which it is directed and not the absolute direction.

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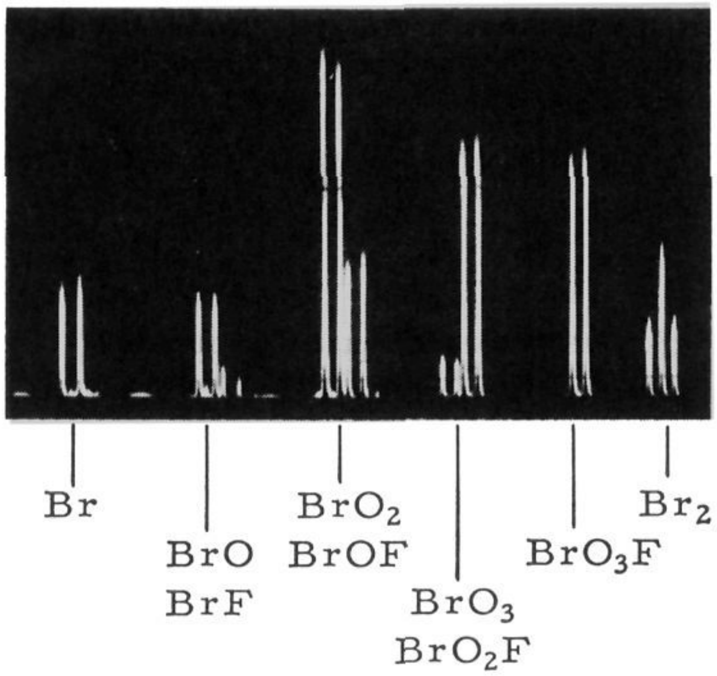

Figure 1. Mass spectrum of perbromyl fluoride.

Perbromyl Fluoride

Sir:

We have synthesized perbromyl fluoride, BrO_3F, by the reaction of potassium perbromate with antimony pentafluoride in anhydrous hydrogen fluoride. It is a highly volatile compound, with a vapor pressure of *ca.* 6 Torr at −80°. At room temperature the compound persists for many weeks in Kel-F or fluorinated metal apparatus, but with evidence of some decomposition or reaction.

The preparation of BrO_3F was suggested by the recent synthesis of stable perbromates[1,2] and by the unusual stability of ClO_3F. The latter has been prepared by direct fluorination of potassium chlorate,[3] and by reaction of potassium perchlorate with HSO_3F,[4] with SbF_5,[5] and with mixtures of the two.[6] More recently it has been made by the reaction of potassium perchlorate with AsF_5 or SbF_5 dissolved in anhydrous HF, BrF_5, or IF_5.[7] Periodyl fluoride, IO_3F, has been reported to result from the passage of fluorine through a solution of periodic acid in HF.[8]

Our experiments leading to the production of perbromyl fluoride were monitored with a time-of-flight mass spectrometer and associated metal vacuum system.[9] Sodium bromate was found to react with elemental fluorine below room temperature to yield Br_2, Br_2O, BrO_2F, BrF_5, and O_2, but not detectable amounts of BrO_3F. Reaction of potassium perbromate with HSO_3F also failed to give BrO_3F, yielding instead Br_2 and O_2.

Perbromyl fluoride was successfully synthesized by a technique analogous to that used by Wamser, *et al.* to prepare ClO_3F.[7] In a typical experiment, 0.2889 g (1.579 mmoles) of $KBrO_4$[2] was placed in a Kel-F tube. The tube was evacuated on a Monel vacuum line and chilled with liquid nitrogen; *ca.* 5 g of HF and 1.2 g of SbF_5 were vacuum distilled into it. The mixture was warmed to room temperature, agitated to dissolve the perbromate, and allowed to stand for 1 hr. The HF and SbF_5 were then removed by absorption on sodium fluoride, leaving 0.0380 ± 0.0005 atm l. of gaseous product at 25°. The product contained no significant quantity of gas that could not be condensed in a liquid nitrogen bath. The condensed product weighed 0.2255 ± 0.001 g, corresponding to a 97% yield of BrO_3F with an apparent molecular weight of 145 ± 2 (calcd 146.9).

Samples of perbromyl fluoride for mass spectrometry were sometimes obtained simply by fractionally distilling the BrO_3F from the original mixture at temperatures between −80 and −100°. Figure 1 shows the mass spectrum of perbromyl fluoride and its fragments. These are readily characterized by the two nearly equally abundant bromine isotopes. Some of the Br_2 may have come from decomposition of the BrO_3F, but more is believed to have arisen from reaction of the compound with incompletely fluorinated surfaces of the spectrometer and its associated vacuum system.

Pure BrO_3F is a colorless gas or liquid solidifying at about −110° to a white solid. However, the solid and liquid are frequently colored yellow by decomposition and/or reaction products. The compound appears to be more reactive than ClO_3F. It hydrolyzes in alkaline solution at room temperature to give fluoride and perbromate.

$$BrO_3F + 2OH^- \longrightarrow BrO_4^- + H_2O + F^-$$

This reaction provides a convenient method of analyzing the compound. Hydrolysis of the 0.2255 ± 0.001 g (1.535 ± 0.007 mmoles) sample mentioned earlier yielded 1.531 ± 0.005 mmoles of BrO_4^- and 1.52 ± 0.02 mmoles of F^-. The reaction consumed 3.11 ± 0.01 mmoles of base. The resulting solution contained only $6.6 \pm 0.2 \times 10^{-3}$ mequiv of oxidizing power attributable to lower oxidation states of bromine.

Detailed studies of the properties of perbromyl fluoride are now in progress. Efforts to synthesize IO_3F from KIO_4 by the analogous method failed to give an identifiable product.

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