significant to notice that the rotatory strengths for the two components of the ${}^1L_b \leftarrow {}^1A$ pair have respective orders of magnitude in the paracyclophane systems that closely correspond to those in the biaryl system of Mislow. The exception is the 240–250-nm band rotatory strength that unequivocally correlates to the absolute inherent dissymmetry in the biaryls. It is an order of magnitude larger than that in the paracyclophane ${}^1L_a \leftarrow {}^1A$ pair.

These observations support a hypothesis that there is less electron exchange in the paracyclophanes than in these biaryls. Thus, for the latter, the concept of an inherently dissymmetric chromophore is the more meaningful, at least for the 240–250-nm band.

A degree of absence of such complications in the paracyclophanes enhances their value as model experimental systems for comparison to simple theory.

Acknowledgment. We wish to thank Union Carbide Corporation for a generous gift of [2.2]paracyclophane, and one of the reviewers for calling our attention to ref 7b.

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Studies in Linear Dichroism. I. Quantitative Evaluation of Linear Dichroic Properties of Molecules in Stretched Polyethylene Films

Sir:

Linear dichroism is normally observed in molecules having a nonrandom organization. Molecules incorporated in stretched polymer films are partially oriented, and hence possess the property of linear dichroism.[1]

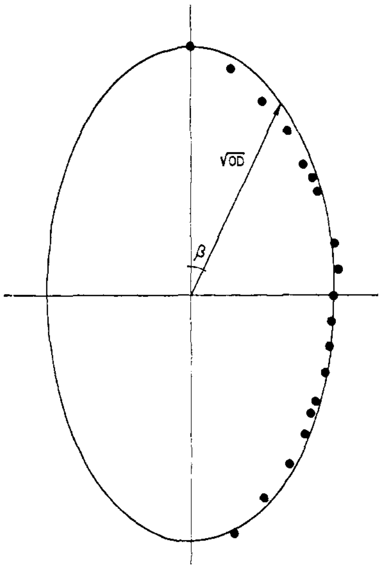

Figure 1. Plot of the square root of the measured optical density at a selected wavelength within the π–π^* transition of Δ^4-cholesten-3-one (III) incorporated into a stretched polyethylene film relative to the angle β in polar coordinates.

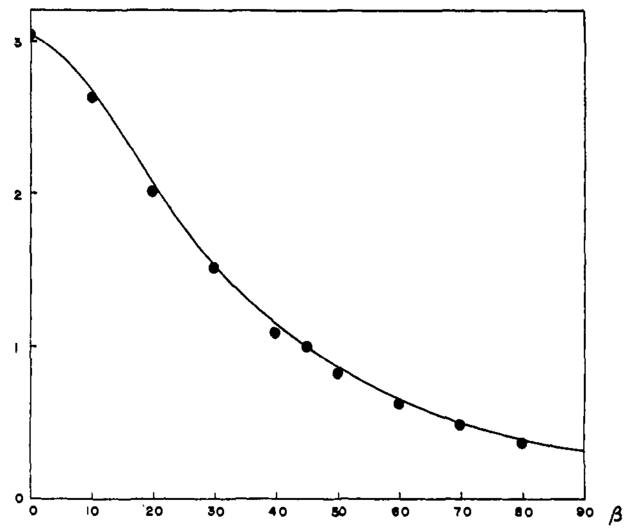

Figure 2. Plot of the dichroic ratio d_β of the π–π^* transition of Δ^4-cholesten-3-one (III) incorporated into a stretched polyethylene film *vs.* the angle β in cartesian coordinates.

Since the absorption of polarized light depends on the square of the scalar product of the transition moment vector of the chromophore and the vector of the electric field of the propagating light, many geometrical properties of the incorporated compounds may be elucidated from linear dichroism measurements, once their orientations are known. We have developed a method which correlates the value of the linear dichroism with the structure of the molecule.

By measuring the uv spectrum with plane-polarized light[2] of various steroidal compounds incorporated in stretched polyethylene films[3] we have observed that the extinction coefficient (ϵ) of light absorbed in the film was dependent on the angle β between the plane of polarization of the light and the direction of stretching of the film. A plot of the square root of the measured optical density (OD) relative to the angle β in polar coordinates gives an ellipse (Figure 1) the axes of which are: $\sqrt{\mathrm{OD}_{\beta=0}}$ and $\sqrt{\mathrm{OD}_{\beta=90}}$. If we define the dichroic ratio as $\mathbf{d}_\beta = \epsilon_\beta/\epsilon_{\beta+(\pi/2)}$, then a plot of this ratio *vs.* β gives a curve which follows directly the curve derived from the same ellipse (Figure 2). Although different ellipses were obtained for different compounds, a few general properties were observed: (a) the value of the dichroic ratio as a function of β was independent of the concentration of the incorporated compound; (b) the dichroic ratio was independent of the degree of stretching.[4] From these observations it is

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[1] (a) R. Eckert and H. Kuhn, *Z. Elektrochem.*, **64**, 356 (1960); (b) H. Jakobi, A. Novak, and H. Kuhn *ibid.*, **66**, 863 (1962), and references therein; (c) L. V. Smirnov, *Optika i Spektroskopiya*, 3, 123 (1957); (d) K. R. Popov, *ibid.*, **3**, 579 (1957); (e) R. D. B. Fraser, *J. Chem. Phys.*, **21**, 1511 (1953); (f) R. D. B. Fraser, *ibid.*, **24**, 89 (1956); (g) R. D. B. Fraser, *ibid.*, **28**, 1113 (1958); (h) R. D. B. Fraser, *ibid.*, **29**, 1428 (1958) (i) A. Kh. Khalilov and G. A. Sultanov, *Izv. Akad. Nauk Azerbaidzhan SSR, Ser Fiz. Tekh., Khim. Nauk*, 35 (1960); (j) Y. Tanizaki, *Bull. Chem. Soc. Japan*, **32**, 75 (1959); (k) Y. Tanizaki and H. Ono, *ibid.*, **33**, 1207 (1960); (l) Y. Tanizaki, *ibid.*, **38**, 1798 (1965); (m) Y. Tanizaki, H. Inoue, and N. Ando, *J. Mol. Spectry.*, **17**, 156 (1965); (n) T. Tsunoda and T. Yamaoka, *J. Polym. Sci., Part A*, **3**, 3691 (1965); (o) J. H. Jaffé, J. Jaffé, and K. Rosenheck, *Rev. Sci. Instr.*, **38**, 935 (1967); (p) K. Rosenheck and B. Sommer, *J. Chem. Phys.*, **46**, **532** (1967); (q) F. Doerr, *Angew. Chem. Intern. Ed. Engl.*, **5**, 478 (1966), and references cited therein.

[2] The instrument used was a dichroism accessory for a Cary Model CD-HC spectrophotometer produced by Rehovoth Instruments Ltd. (For a description see ref 1o.) The polyethylene films used were Suprathen 100 & 200. Grateful acknowledgment is made to Kalle and Co. AG. for kindly supplying the polymer sheet used in the work.

[3] For the method of incorporation see A. Yogev, J. Riboid, J. Marero, and Y. Mazur, *J. Am. Chem. Soc.*, **91**, 4559 (1969).

[4] This can be understood from the stress–strain curve of polyethylene. Since commercial polyethylene films are partially oriented in

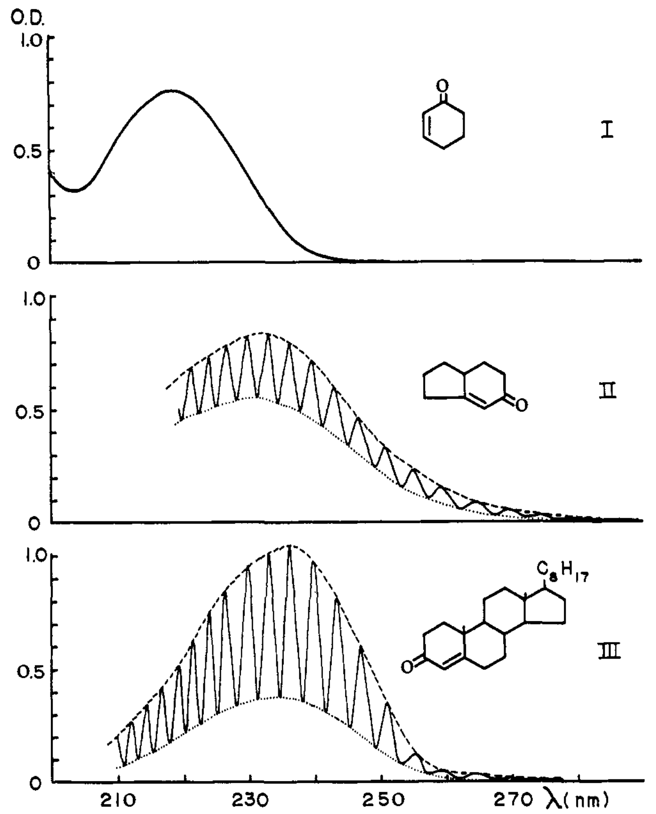

Figure 3. The linear dichroic curve of I, II, and III measured with CD-HC accessory:[10] (- - -) the curve of the interpolated optical densities obtained by light polarized in the direction of stretching; (· · ·) the curve obtained by light polarized perpendicular to the direction of stretching.

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-

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

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.

(7) C. P. Scott Research Fellow of the Weizmann Institute of Science.

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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.

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

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.

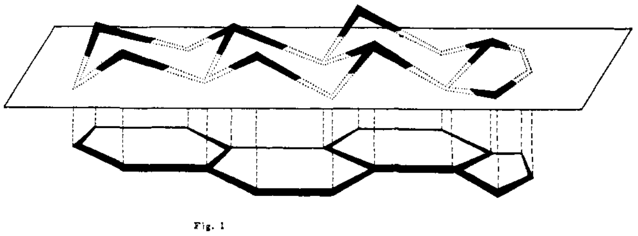

Figure 1. Projection of a steroid molecule on a dissecting plane.

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).