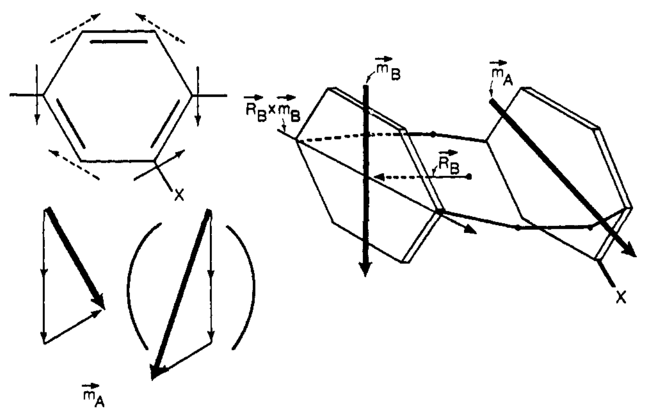

Figure 1. Vector constructions relating paracyclophane absolute configuration to ${}^1L_b \leftarrow {}^1A$ rotatory strength. Substituent spectroscopic moments are shown on the left as full arrows. They contribute in a fashion that depends on location of the substituent (full arrows) and the magnitude and sign given to the spectroscopic moment. The net transition vector dipole $\vec{m}_A$ is given for arbitrary magnitudes and a positive (negative) substituent spectroscopic moment. The vector cross-product on the right has a resultant directed in a right-handed sense.

strengths associated with the dipole strengths of eq 3 are[10]

$$\begin{aligned} R_{0,\pm} &= -i\vec{m}_{0,\pm}\cdot\mu_{\pm,0} \\ &= \pm\pi\tilde{\nu}_{0i}\vec{m}(\mathrm{A})_{0i}\cdot\vec{R}(\mathrm{B}) \times \vec{m}(\mathrm{B})_{0i} \qquad (5) \end{aligned}$$

where $\tilde{\nu}_{0i}$ is the frequency in cm^{-1} of the zero-order $i \leftarrow 0$ transition and use has been made of the relationship $\vec{p}_{0i} = (-2\pi imc/e)\tilde{\nu}_{0i}\vec{m}_{0i}$. Some elaboration by adding special Franck–Condon overlap factors to eq 3 and 5 is necessary to account for lowest order vibronic coupling effects.[11]

The polarizations and magnitudes represented by the electric moments $\vec{m}_{0i}(\mathrm{A})$ and $\vec{m}_{0i}(\mathrm{B})$ for ${}^1L_b \leftarrow {}^1A$ in eq 3 and 5 can be inferred from Platt's semiempirical theory of spectroscopic moments for substituted benzenes.[5] Figure 1 shows the relevant vector constructions.

The theory affords a quantum mechanical assignment of the *absolute configuration* that is in agreement with the experimental assignment.[12] The theory suggests, and experimental examples[13] have confirmed, that *for the given absolute configuration, the sign of the longest wavelength singlet–singlet CD of the transition pair follows* (*and will be opposite to*) *that of the signed parameter, the spectroscopic moment of its substituent.* As Figure 1 shows, the out-of-phase, then in-phase (going to higher frequency) combination of benzene electric moments for the two states results in a reversal of the projection of vector $\vec{R}(\mathrm{B}) \times \vec{m}(\mathrm{B})_{0i}$ on $\vec{m}(\mathrm{A})_{0i}$ while preserving the projection magnitude. The initial sign of this projection depends on the spectroscopic moment for the additional substituent on A through its contribution to $\vec{m}(\mathrm{A})_{0i}$.

Platt's work suggests that this scheme will fail for the ${}^1L_a \leftarrow {}^1A$ related transitions where significantly large experimental intensity changes are not observed. Indeed, on theoretical grounds Moffitt[14] points out that ${}^1L_a \leftarrow {}^1A$ bands are expected to be insensitive to inductive effects relative to the ${}^1L_b \leftarrow {}^1A$ bands. On the other hand, the former bands are expected to be the *more* sensitive to vibronic coupling effects.

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(10) See also: H. Eyring, J. C. Liu, and D. Caldwell, *Chem. Rev.*, **68**, 525 (1968); J. A. Schellman, *Accounts Chem. Res.*, **1**, 144 (1968).

(11) O. E. Weigang, Jr., *J. Chem. Phys.*, **43**, 71 (1965).

(12) H. Falk and K. Schloegel, *Angew. Chem. Int. Ed. Engl.*, **7**, 383 (1968).

(13) M. J. Nugent and O. E. Weigang, *J. Amer. Chem. Soc.*, **91**, 4556 (1969).

(14) W. Moffitt, *J. Chem. Phys.*, **22**, 320 (1954).

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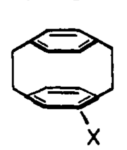
[2.2]Paracyclophane System Optical Activity. II. Circular Dichroism of Ring-Substituted Paracyclophanes[1]

Sir:

The ring-substituted paracyclophanes afford the rare opportunity[2] to compare observed optical activity to the parameters of a simple theory.[3] The optically active 4-substituted [2.2]paracyclophanes **1** used in this study,



1a X = CO_2H
1b X = CH_3
1c X = CH_2Br
1d X = CH_2OH

with the exception of 4-methyl[2.2]paracyclophane (**1b**), have been described previously.[4] However, neither their circular dichroism (CD) nor optical rotatory dispersion has been reported.

The absolute configuration of (+)-(*S*)-4-carboxy-[2.2]paracyclophane has been assigned to **1a** by kinetic arguments.[5] The prediction of its absolute configuration by a semiempirical exciton theory[3] is found to be successful. This communication examines the correspondence of the experimental data for **1** to this and other details of the theory.

With the exception of the methyl derivative, the CD measurements were carried out on derivatives of (+)-(*S*)-4-carboxy[2.2]paracyclophane (**1a**) that therefore have the *S* configuration. (−)-(*R*)-4-Methyl-[2.2]paracyclophane, enantiomeric to **1b**, was derived from (−)-(*R*)-acid.[6] The (−)-(*R*)-methyl derivative, derived from 92% optically pure (−)-(*R*)-acid, had $[\alpha]^{25}\mathrm{D}$ −75.0° (*c* 4.0, chloroform), mp 150–151°, and gave satisfactory analysis.

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(1) This work supported by Public Health Service Grant GM 11644.

(2) See also the systems considered by: S. F. Mason and G. W. Vane, *J. Chem. Soc.*, *B*, 370 (1966); S. F. Mason, G. W. Vane, K. Schofield, R. J. Wells, and J. S. Whitehurst, *ibid.*, 553 (1967).

(3) M. J. Nugent and O. E. Weigang, Jr., *J. Amer. Chem. Soc.*, **91**, 4555 (1969).

(4) D. J. Cram and N. C. Allinger, *ibid.*, **77**, 6289 (1955); D. J. Cram, and L. A. Singer, *ibid.*, **85**, 1078 (1963).

(5) H. Falk, and K. Schloegel, *Angew. Chem. Int. Ed. Engl.*, **7**, 383 (1968).

(6) (−)-(*R*)-4-Methyl[2.2]paracyclophane was prepared by treatment of (+)-(*R*)-4-bromomethyl[2.2]paracyclophane with sodium and *t*-butyl alcohol in tetrahydrofuran. *Cf.* P. G. Gassman and P. G. Pape, *J. Org. Chem.*, **29**, 160 (1964).

Figure 1 shows the qualitative characteristics of eq 3 and 5 of ref 3, transition pairs where the CD suggests equal magnitude but opposite sign rotatory strengths whose corresponding dipole strengths are distinctly unequal. The absorption region of the first pair falls between 280 and 330 nm and can be correlated to the ${}^1L_b \leftarrow {}^1A$ benzene transition. The first member of the second pair is located between 250 and 280 nm; the second member when observable is between 220 and 250 nm. The second pair correlates to the ${}^1L_a \leftarrow {}^1A$ benzene transition.

Considering the long-wavelength transition pair derived from the benzene ${}^1L_b \leftarrow {}^1A$ monomer transition, Figure 1 shows the acid **1a** to have a positive–negative (going to higher frequencies) CD transition pair. The ordinary absorption gives poor definition of the second band on the rising background of the higher more intense transitions.

Platt's spectroscopic moment[7] for the -COOH substituent (Table I) is negative (ref 3, Figure 1). The out-of-phase and therefore longer wavelength combination of net ring moments for the two phenyl groups unambiguously yields a rotatory strength that is positive, as is observed. Note that the out-of-phase combination implies taking the negative sign for eq 5 of ref 3 and the sign of the triple scalar product from Figure 1 of ref 3.

Table I. Platt's Spectroscopic Moments

Substituent	Spectroscopic moment[a]
CH_3	7
Alkyl bridge	5[b]
CH_2OH	-7[c]
CH_2Br	-12[c]
COOH	-28

[a] Reference 7. [b] Set equal to moment for C_2H_5. [c] Sign and magnitude are regarded as less certain but most probable in ref 7.

The (+)-(*S*)-methyl compound **1b** shows the now negative–positive CD pair that theory associates with change in sign of the methyl-substituent spectroscopic moment. The second band, not completely resolved in the CD, is in this case clearly discernible in the ordinary absorption since the higher transitions are blue shifted relative to the acid.

The bromomethyl substituent in **1c** produces a positive long-wavelength CD that is consistent with its assigned spectroscopic moment. The second band cannot be discerned in the ordinary absorption, but the minimum of the CD in this region corresponds to its location as suggested by the nearly uniform split interval in the other compound spectra.

Finally, the hydroxymethyl substituent in **1d** gives a positive–negative pattern opposite in sign but equal in magnitude to that for the methyl compound. This is entirely consistent with the spectroscopic moment for $-CH_2OH$ which is opposite in sign but equal in magnitude to that for $-CH_3$.[7b]

The ${}^1L_a \leftarrow {}^1A$ pair in contrast shows the *same pattern of rotatory strength signs* for a given absolute configuration, regardless of substituent moment. The result is not unexpected.[3]

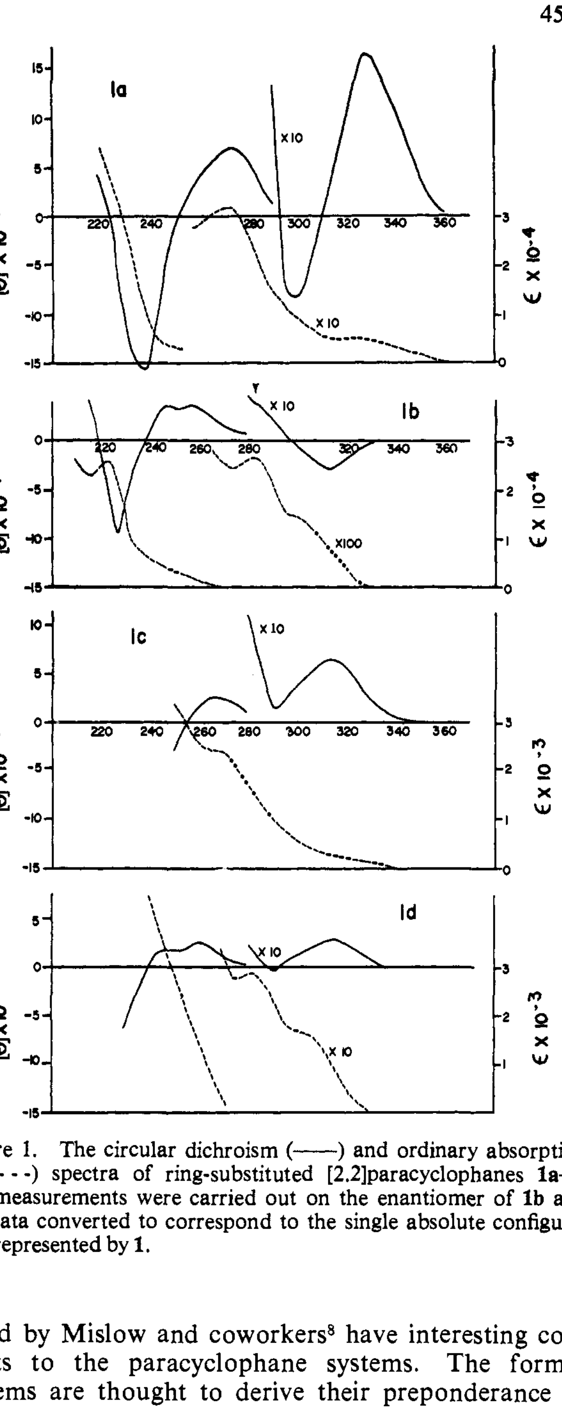

Figure 1. The circular dichroism (——) and ordinary absorption (------) spectra of ring-substituted [2.2]paracyclophanes **1a–d**. CD measurements were carried out on the enantiomer of **1b** and the data converted to correspond to the single absolute configuration represented by **1**.

The type of biaryl compounds that have been investigated by Mislow and coworkers[8] have interesting contrasts to the paracyclophane systems. The former systems are thought to derive their preponderance of rotatory strength from an "inherently dissymmetric" (C_2 point group) biphenyl chromophore system. Thus the "inductive" (in the largest sense) turning of transition dipole moments to obtain optical activity in the paracyclophane systems is to be contrasted to a conformational turning in the biphenyls, *i.e.*, the increase from zero of the dihedral angle between the biphenyl rings. As well, certain terms neglected in eq 5 of ref 3 may now be significant.

The addition of substituents that serve to fix the absolute configuration and the inherent dissymmetry in the biaryl systems of Mislow undoubtedly also exert strong "inductive" influences that must be considered in the interpretation of the ${}^1L_b \leftarrow {}^1A$ pair.[9] It is

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(7) (a) J. R. Platt, *J. Chem. Phys.*, **19**, 263 (1951); (b) J. Petruska, *ibid.*, **34**, 1120 (1961).

(8) K. Mislow, E. Bunnenberg, R. Records, K. Wellman, and C. Djerassi, *J. Amer. Chem. Soc.*, **85**, 1342 (1963); K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss, and C. Djerassi, *ibid.*, **84**, 1455 (1962).

(9) S. F. Mason, *Quart. Rev.* (London) **17**, 20 (1963).

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]

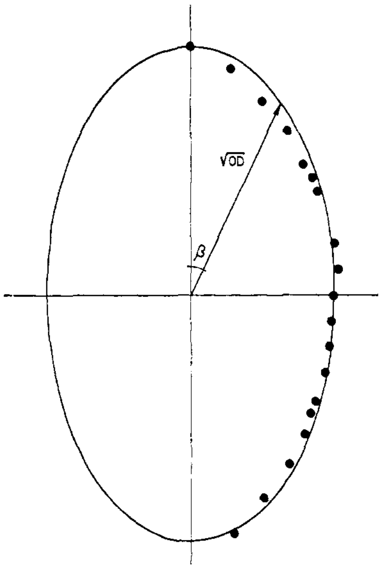

Figure 1. Plot of the square root of the measured optical density at a selected wavelength within the π–π^* transition of Δ^4-cholesten-3-one (III) incorporated into a stretched polyethylene film relative to the angle β in polar coordinates.

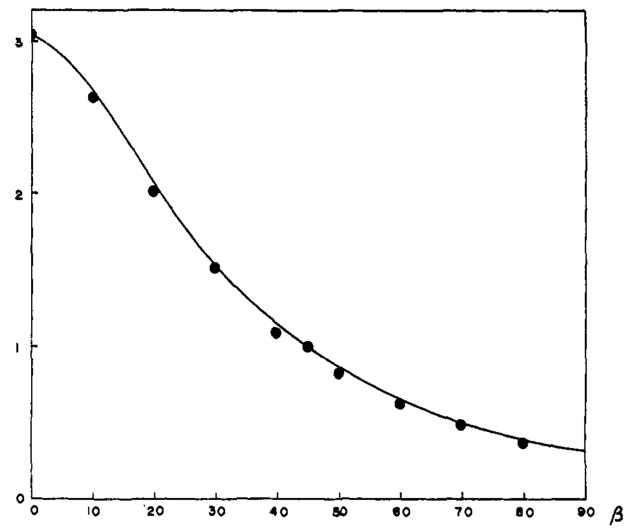

Figure 2. Plot of the dichroic ratio $\mathbf{d}_\beta$ of the π–π^* transition of Δ^4-cholesten-3-one (III) incorporated into a stretched polyethylene film *vs.* the angle β in cartesian coordinates.

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