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SOME APPLICATIONS OF THE KRONIG-KRAMERS THEOREM TO OPTICAL ACTIVITY

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IN general, the speed of a light wave traversing a material medium will be different from its speed in vacuum, and the intensity of the wave will decrease with the distance traveled. The extent to which these phenomena manifest themselves will depend, *inter alia*, upon the frequency ν of the light wave. As is well known, it is a consequence of the geometrical dissymmetry of so-called optically active molecules that the magnitudes of these dispersive and absorptive effects will be different for left and right circularly polarized light in media which contain such molecules. This condition obtains even in homogeneous, isotropic solutions (and our subsequent remarks will be confined to materials of this sort) with the result that such solutions exhibit both circular birefringence and circular dichroism.

Subject to very general assumptions, it may be shown that the dispersive and absorptive effects associated with ordinary (as opposed to rotatory) phenomena are not entirely independent and that from a knowledge of either one of them over the entire region of the spectrum ($\lambda = 0 \rightarrow \lambda = \infty$) one can in fact predict the other. This statement, which will be recognized as a form of the Kronig-Kramers theorem,[1] holds not only for the experimentally observed cumulative absorptions and dispersions, but also for the partial absorption and partial dispersion associated with any particular electronic transition. Physically, of course, this is quite reasonable since both the dispersive and absorptive phenomena take their origins, respectively, in the in-phase and out-of-phase components of the same electronic charge displacements which are induced by the periodic electromagnetic fields associated with the light wave.

The remarks of the preceding paragraph apply also to circular birefringence and circular dichroism with the result that much of the formalism of ordinary and rotatory phenomena is quite similar. This is indicated more explicitly in the outline shown in Table 1.

The important quantity on the rotatory side in Table 1 is R_K, the rotational strength of the K^{th} electronic transition. As has been noted elsewhere,[5] it is R_K that gauges in both sign and magnitude the contribution of an electronic transition to both the rotatory dispersion and the circular dichroism and hence acts as the signed scaled factor that determines how strongly a particular electronic promotion takes part in phenomena associated with optical activity. In addition, as explained below, its value will mirror to a certain extent the nature of the chromophore whose transitions are involved.

Prima facie, one might expect $R_K = \mu_e{}^K \cdot \mu_m{}^K$ to be of the order of a Debye times a Bohr magneton, i.e. $\sim 10^{-38}$ cgs. This is indeed the case when the chromophore

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[1] R. de L. Kronig, *J. Opt. Soc. Amer.* **12**, 547 (1926); H. A. Kramers, *Atti congr. intern. fisici*, *Como* **2**, 545 (1927); For a review with extensive references see J. R. Macdonald and M. K. Brachman, *Rev. Mod. Phys.* **28**, 393 (1956).

TABLE 1

Ordinary phenomena	Rotatory phenomena
(1) Partial absorption band associated with the K^th transition can be characterized in terms of three parameters (a) wave length of maximum absorption: λ_K (b) a measure of the halfwidth: Δ_K (c) a measure of the area or intensity, the dipole strength: D_K $D_K = \frac{3hc}{8\pi^3 N_1}\int_0^\infty \frac{k_K(\lambda)}{\lambda}\,d\lambda$ Here $k_K(\lambda)$ is the partial absorption coefficient for the K^th transition. The total mean of absorption coefficient $k = \sum_K k_K(\lambda)$.	(1) Partial dichroism band associated with the K^th transition can be characterized in terms of three parameters (a) wave length of maximum ellipticity: $\lambda_K{}^\circ$ (b) a measure of the halfwidth: $\Delta_K{}^\circ$ (c) a measure of the area or intensity, the rotational strength: R_K $R_K = \frac{3hc}{8\pi^3 N_1}\int_0^\infty \frac{\theta_K(\lambda)}{\lambda}\,d\lambda$ Here $\theta_K(\lambda)$ is the partial ellipticity associated with the K^th transition; N_1 is the number of active molecules per cm^3.
(2) D_K is calculated as the absolute value squared of the electric dipole moment matrix element for the K^th transition. We shall abbreviate this as: $D_K = \mu_e{}^K \cdot \mu_e{}^K$	(2) R_K is calculated as the imaginary part of the dot product of the electric dipole moment matrix element times the magnetic dipole moment matrix element (exclusive of spin) for the K^th transition. We indicate this as: $R_K = \mu_e{}^K \cdot \mu_m{}^K$
(3) The real and imaginary parts of the index of refraction or dielectric constant related by the Kronig-Kramers Theorem.	(3) Real and imaginary parts of optical activity (circular birefringence and circular dichroism, respectively) related by a pair of Kronig-Kramers type reciprocal relationships.

itself is inherently dissymmetric (e.g. hexahelicene).[2] However, when the chromophore possesses some higher intrinsic symmetry (e.g. the carbonyl group, which has two orthogonal reflection planes) then most often to a first approximation the transitions of the chromophore will be either electric dipole allowed or magnetic dipole allowed, but not both. It is the latter type of transition (i.e. where $\mu_e{}^K = 0$ to the lowest order of approximation) that lends itself most readily to study by experimental polarimetry. In such instances the optical activity arises through an unsymmetrical perturbation of the chromophoric electrons by a dissymmetric molecular environment in such a way as to provide a small, but nonzero, value for the contribution of $\mu_e{}^K$ to the induced electric dipole moment. In these cases, $\mu_e{}^K$ will be much less than a Debye and the value of R_K will be less than 10^{-38} cgs by perhaps two orders of magnitude or more.

We shall now consider specific calculations involving the two types of chromophores discussed above:

Case I—The essentially dissymmetric chromophore

Example. Hexahelicene. When the chromophore is of the inherently dissymmetric type, it can be shown that the shape of the absorption curve and the shape of the dichroism curve must be the same.[3b] Hence, if the rotational strengths can be calculated and if the absorption spectrum be available, one should be able to calculate the

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[2] M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.* **78**, 4765 (1956).

actual shape of the rotatory dispersion curve by means of the reciprocal relations relevant to optical activity. We have performed such a calculation for the molecule hexahelicene,[2] which, as you know, is an aromatic hydrocarbon consisting of six benzenoid rings fused into a roughly helical form.

At the April 1958 ACS meeting in San Francisco we presented our results for the calculation of the rotatory dispersion of hexahelicene in the region from 14,000 to 27,000 cm^{-1}. For that calculation[3a,b] no knowledge of the shape of the dichroism is necessary, for the region considered is sufficiently far removed from any band center that each partial rotation is of the Drude form, and the specific rotation [α] may be calculated from the Rosenfeld equation

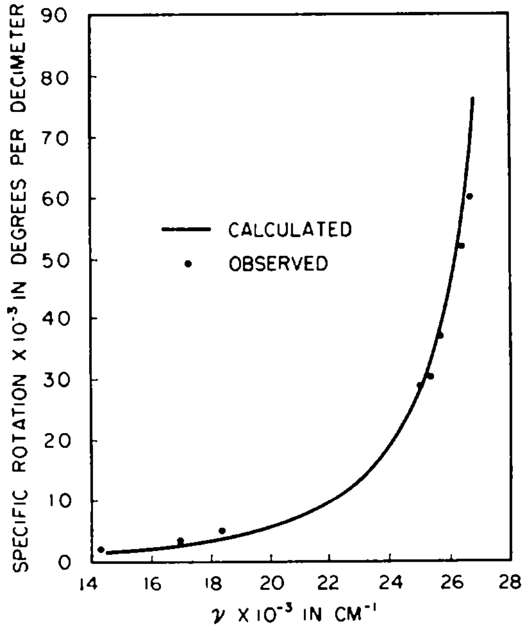

Fig. 1. Rotatory dispersion of hexahelicene (in chloroform)

$$[\alpha] = A \sum_K R_K \frac{\nu^2}{\nu_K{}^2 - \nu^2} \cdot \frac{n^2 + 2}{3},$$

where A is a known constant, ν_K is the frequency corresponding to the K^{th} transition, and n is the index of refraction of the medium.

Naturally, such a calculation entails certain approximations, and I'll be happy to discuss these during the question period. For the time being, suffice it to say that the wave functions necessary for the computation were obtained from simple Hückel molecular orbital theory and that aside from the need to know the geometry of the molecule and the value of spectroscopic β that enters into Hückel theory, the calculation is a completely *a priori* one. [For another approach to this problem, see D. D. Fitts and J. G. Kirkwood, *J. Am. Chem. Soc.* 77, 4940 (1955)].

The results are shown in Fig. 1. The agreement between theory and experiment

[3a] A. Moscowitz and J. de Heer, *Division of Physical and Inorganic Chemistry, American Chemical Society Meeting* Paper 25. San Francisco, April (1958). [b] A. Moscowitz, Doctoral Thesis, Harvard University (1957).

was sufficiently encouraging to tempt us to extend the calculation into regions of resonance absorption by the method of using the reciprocal relations, as mentioned above.

For the purposes of the extended calculation, the experimental absorption curve, which was supplied to us by Professor Melvin Newman and Dr. Lini Tsai of Ohio State, was approximated by a sum of three curves Gaussian in frequency corresponding to three optically active transitions, as shown in Fig. 2. The results of the computations are shown in Fig. 3 along with the experimental data supplied to us by Drs. Newman and Tsai. (It should be mentioned here that the experimental absorption data were taken with cyclohexane as solvent, but that chloroform is the solvent in the case of the rotation data. This multiplicity of solvents is unfortunate.)

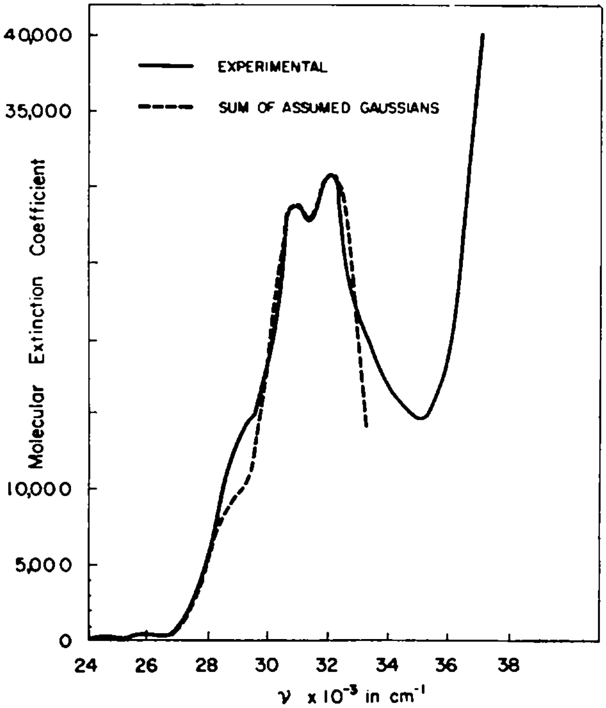

FIG. 2. Absorption spectrum of hexahelicene (in cyclohexane)

The agreement between theory and experiment is good, especially in view of the approximations that go into the calculation. However, it should be pointed out that because of the large amount of overlapping of the absorption bands under consideration, no unique breakdown into a sum of Gaussians is possible, although the allowed range of possibilities is somewhat limited. As such, the calculation doesn't represent an unequivocal test of the theoretical principles involved. Nevertheless, it is gratifying to note that one can at least achieve a reasonable simultaneous fit to both the absorption and the dichroism where theory predicts that one should exist. And the calculation does provide a further confirmation of the validity of the rotational strengths as computed from simple molecular orbital theory.

It is well to point out here the similarity of our approach to that used by Professor

Kuhn in some of his own calculations. Not only the approach, but the very forms of some of the equations turn out to be quite similar to his, although not identical. This is not mere coincidence, for as Condon[4] has pointed out, the ratio of quantum mechanical quantities, R_K/D_K, which enters into the calculation is closely related to Professor Kuhn's anisotropy factor. Moreover, Professor Kuhn's approach to the problem of the relationship between the shape of the partial rotatory dispersion curve and the shape of the associated partial dichroism and absorption curves can be shown to be closely related to the general techniques which employ the integral transform relations if the transitions involved are electric dipole allowed. However, we feel his approach does have restricted validity if such is not the case, as for example in the saturated ketones, which we discuss now.

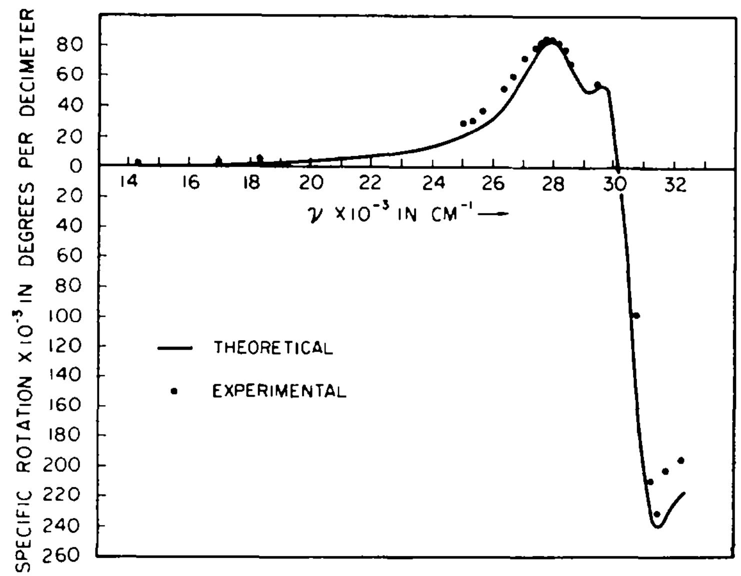

Fig. 3. Rotatory dispersion of hexahelicene (in chloroform)

Case II—*The symmetric chromophore*

Example. The saturated ketones. As noted previously, when the chromophore possesses higher symmetry and is situated in a symmetric molecular environment, as is the carbonyl group in, say, formaldehyde, its associated transitions will be optically inactive. However, if the rest of the molecule be dissymmetrically disposed with respect to such a chromophore (e.g., as in a steroid) then the effect of the environment is to induce a dissymmetry in the electron distribution within the chromophore with the result that its transitions become optically active. In such instances, the rotational strengths for the chromophoric transitions take on an added importance, for they then serve to measure the chromophore's interaction with its dissymmetric molecular environment. Hence, the variation in the rotational strength of a particular transition of a chromophore from molecule to molecule should be fraught with important structural information. And the recent work of Djerassi, Klyne, Schellman and

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[4] E. U. Condon, *Rev. Mod. Phys.* 9, 432 (1937).

others at this symposium has provided ample empirical justification for this point of view.

The first step in the formulation of an organized program to implement these ideas would be to obtain fairly good empirical values for the rotational strengths from the existing dispersion data. The late Professor William Moffitt and I, in close cooperation with Dr. Djerassi, undertook to solve this phase of the problem and we have developed several graphical and computational procedures that will do the job. These entail varying amounts of labor and achieve varying degrees of accuracy. At present we feel that a computational procedure worked out while I was a guest of the Bell Telephone Laboratories and had access to their IBM 704 computer, represents the most satisfactory compromise between tractability and accuracy. Details of the procedure may be found in Dr. Djerassi's book.[5] Just let me say at this point that the method uses the reciprocal relations in conjunction with a least squares curve fitting process for nonlinear functions to pick out, subject to the assumptions inherent in the procedure, the single dichroism curve Gaussian in wave length which best satisfies the data subject to the criterion of least squares. The rotational strength may be determined from the parameters of this curve. Two successful examples of the results of the curve fitting process are shown in Figs. 4 and 5.

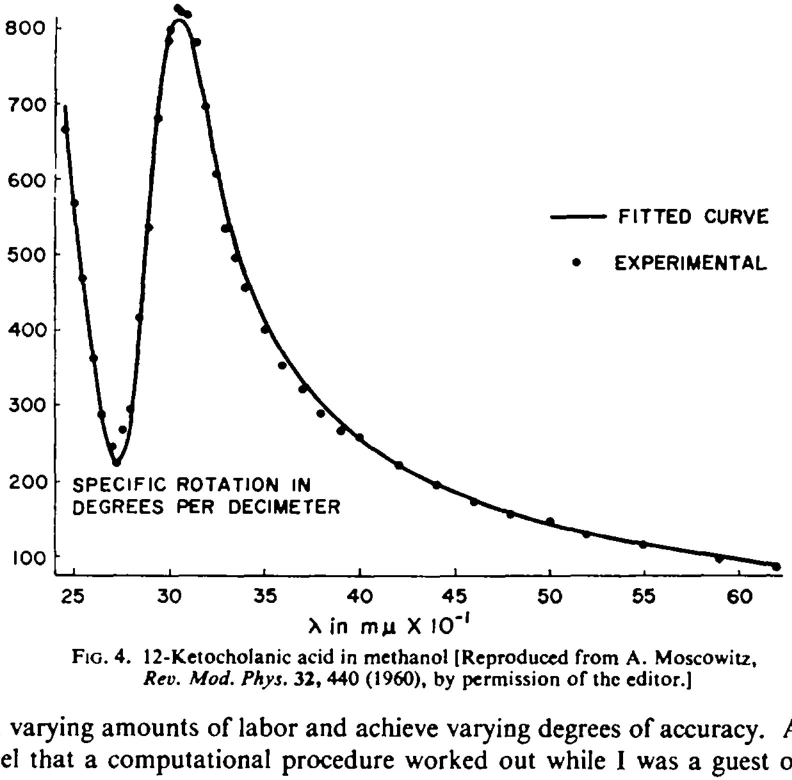

FIG. 4. 12-Ketocholanic acid in methanol [Reproduced from A. Moscowitz, *Rev. Mod. Phys.* **32**, 440 (1960), by permission of the editor.]

It might be well to point out here that in a series of similar compounds the half widths of the best single Gaussians may lie between fairly narrow limits. For example, in most of the saturated ketones we examined, the Δ's for the 290 mμ transition fell between about 18 and 21 mμ. Moreover, in these compounds, the next higher transition is some 90 mμ toward the ultraviolet, so that the background rotation

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[5] C. Djerassi, *Optical Rotatory Dispersion* Chap. 12. McGraw-Hill, New York (1960).

contributed by all the transitions other than the one under surveillance will usually have a relatively small curvature in the region between the peak and the trough of the partial dispersion curve associated with the 290 mμ transition. These two facts taken together allow one to show that there will be a rough proportionality between rotational strengths and molecular amplitudes. Advantage was taken of this proportionality in testing the octant rule, already mentioned by Dr. Djerassi in his talk, on a semi-quantitative basis by using molecular amplitudes.

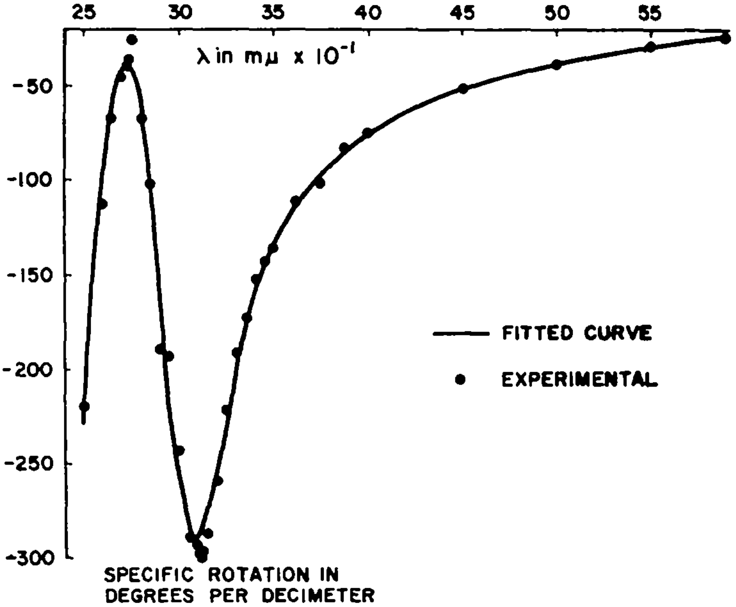

FIG. 5. 3-Acetoxy-cholestan-7-one in methanol [Reproduced from A. Moscowitz, *Rev. Mod. Phys.* 32, 440 (1960), by permission of the editor.]

Of course, what is ultimately desired is a complete quantitative treatment of the octant rule. And for this we must examine the orbitals involved in the transition. Since the work of McMurry and Mulliken[6], and later Pople and Sidman[7], it has been fairly well established that the 290 mμ transition in saturated ketones involves, roughly speaking, the promotion of an electron from an essentially nonbonding 2p orbital situated on the oxygen atom to an antibonding π orbital involving both the carbon and the oxygen of the carbonyl group. The relevant orbitals are sketched in schematic fashion in Fig. 6.

As Dr. Kauzmann and Dr. Eyring[8] realized twenty years ago, a situation like this is best treated in terms of the one-electron theory. To a first approximation the transition is electric dipole forbidden so that μ_e^1 for the transition will be zero to this order of approximation, although μ_m^1 will be of the order of a Bohr magneton. Here we have set the superscript K = 1 since the transition we are discussing is the first to

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[6] H. L. McMurry and R. S. Mulliken, *Proc. Natl. Acad. Sci. Wash.* 26, 312 (1940); H. L. McMurry, *J. Chem. Phys.* 9, 231 (1941).

[7a] J. W. Sidman, *J. Chem. Phys.* 27, 429 (1957); [b] J. A. Pople and J. W. Sidman, *Ibid.* 27, 1270 (1957); [c] J. W. Sidman, *Chem. Rev.* 58, 689 (1958).

[8] W. J. Kauzmann, J. E. Walter and H. Eyring, *Chem. Rev.* 26, 339 (1940).

appear on the long wave length side of the spectrum. The essential point then is to consider in what manner a component of μ_e^1 can be induced in the direction of μ_m^1. This can be brought about in the quantum mechanical formalism by allowing the excited state orbital, which in the coordinate system chosen is formed from a linear combination of $2p_x$ atomic orbitals of carbon and oxygen, to take on some of the characteristics of still higher lying orbitals (e.g. $3d_{yz}$ orbitals) under the action of the dissymmetrically disposed vicinal atoms. The entire excited state molecular orbital so formed will then be neither symmetric nor antisymmetric with respect to the symmetry planes of the carbonyl group and hence $\mu_e^1 \cdot \mu_m^1$ will no longer be zero.

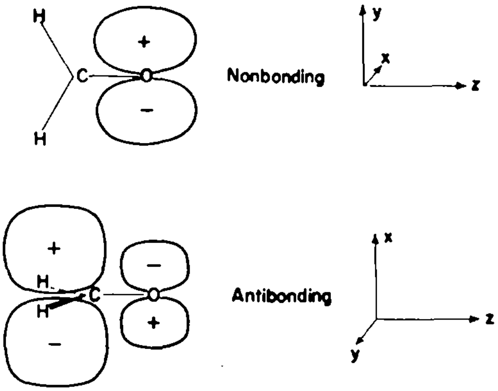

FIG. 6. Diagrammatic representation of the orbitals involved in the 290 mμ carbonyl transition (shown for formaldehyde). [Reproduced by permission from *Optical Rotatory Dispersion* by C. Djerassi. McGraw-Hill, New York (1960).]

A detailed examination shows that if the perturbations produced by the vicinal atoms are spherically symmetric about their own atomic centers, then these perturbations are ineffective if the atoms lie in one of the symmetry planes of the carbonyl group. If the atom does not lie in such a plane, the sign of its perturbation contribution to μ_e^1 will depend upon in which of the four quadrants determined by symmetry planes it lies. A third surface exists which will further divide the quadrants into the eight sign-determining regions which form the basis of the octant rule mentioned by Dr. Djerassi. The exact geometry of this surface will depend upon the relative interactions of the perturbing vicinal atoms with the carbon and the oxygen that comprise the carbonyl group. For the present, this surface is approximated by a third plane perpendicular to the symmetry planes midway along the C═O bond to achieve the eight octants of the present formulation of the octant rule. However, the third surface is most probably not planar in form.

The calculations in which we are presently engaged should shed some more light on the nature of this surface. I had hoped to be able to report on some actual results of the quantitative treatment of the octant rule at this meeting. Unfortunately, at the time I left Minnesota we were still a few weeks away from applying these ideas quantitatively to an actual molecule. All the relevant molecular integrals have been evaluated for the case of perturbing carbon and hydrogen atoms, and it is now just a matter of combining them properly to form the matrix elements pertinent to the geometries of a series of actual molecules. The perturbation we have invoked is that of the incomplete screening of the nuclei of the vicinal atoms as suggested by the work of Condon *et al.*[9]

As I have already intimated, I think the origins of many of the ideas I have mentioned here can be found in the early work of Condon, Kauzmann and Eyring. At the time at which they worked on the carbonyl problem, the carbonyl orbitals were not sufficiently well characterized nor was there the valuable experimental data available that we have today. The former handicap has been overcome through the work of McMurry and Mulliken and the latter handicap has been removed through the work of Djerassi, Klyne, and others present here today. As such, it may be possible to put the octant rule on a firm quantitative basis. This could lead to a useful set of rules for the structural chemist and would at the same time allow the theoretician to decide which are the important intramolecular forces that give rise to optical activity of the sort just discussed.

TABLE 2

Compound (in methanol, except where noted)	Exptl. $[R_1]$	Calc. $[R_1]$
2,5-dimethyl-cyclohexanone[a]	+1·8	+1·4
2,2,5-trimethyl-cyclohexanone[a]	+6·7	+6·6
trans-9-methyl-1-decalone (dioxane)[b]	−2·7	+3·3
trans-9-methyl-3-decalone (dioxane)[b]	−3·6	−2·1
cis-9-methyl-6-decalone[b]	+0·73	+1·1
1β:9β-dimethyl-*trans*-decalone-3	−0·70	−0·73
cis-10-methyl-1-decalone	−0·74	−0·75
8β,9β-dimethyl-*trans*-decalone-2	+5·1	+5·1

[a] From unpublished data of Djerassi, Osiecki and Eisenbraun

[b] Parameters fixed with these compounds

Note added in proof: Since the time of the meeting, the calculations for a quantitative treatment of the octant rule outlined under Case II in the manuscript have been carried out for a number of saturated ketones in collaboration with Dr. L. C. Snyder of the Bell Telephone Laboratories. The results, which represent work which is only exploratory in nature and which should be considered as only tentative, nevertheless seemed gratifying enough to be worth mentioning here. We have used effective nuclear charges of 1·2 and 1·5 for carbon and oxygen, respectively, in the π-antibonding orbital together with Sidman's coefficients, and we have used an effective charge of unity for both the carbon and oxygen d orbitals. In addition to the effective nuclear charges for the π-orbital, two other parameters were necessary, and these were all determined empirically. Solvent effects were ignored. With these considerations, Dr. Snyder and I find the results indicated in Table 2. The experimental values were obtained from the data of DJERASSI and coworkers by means of the curve fitting procedure already described. The units are those of reduced rotational strength as given in Chapter 12 of Djerassi's book.

[9] E. U. Condon, W. Altar and H. Eyring, *J. Chem. Phys.* **5**, 753 (1937).