[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA, MINNEAPOLIS 14, MINN., OF NEW YORK UNIVERSITY, NEW YORK 53, N. Y., OF STANFORD UNIVERSITY, STANFORD, CALIF., AND FROM THE BELL TELEPHONE LABORATORIES, MURRAY HILL, N. J.]

Optical Rotatory Dispersion Associated with Dissymmetric Non-conjugated Chromophores. An Extension of the Octant Rule[1-3]

BY ALBERT MOSCOWITZ, KURT MISLOW, M. A. W. GLASS AND CARL DJERASSI

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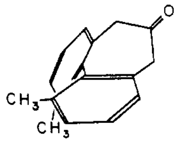
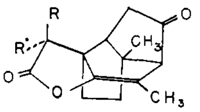
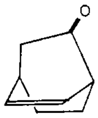
It is shown that the effect on the long-wave length carbonyl transition of ethylenic and aromatic moieties, such as occur in β,γ-unsaturated ketones, merits treating the composite carbonyl–carbon–π system as an inherently dissymmetric chromophore. This represents a shift in viewpoint from the theoretical considerations used in enunciating the original octant rule, which dealt exclusively with an asymmetrically perturbed, intrinsically symmetrical chromophore. It is shown that this shift in viewpoint is of advantage in understanding the optical properties of β,γ-unsaturated ketones and often allows one to make ready determinations of absolute configuration or conformation.

It has been pointed out[4] that (+)-dimethyldibenzsuberone (I) not only exhibits a Cotton effect of high amplitude, but that the long-wave length carbonyl absorption displays the enhanced intensity which characterizes β,γ-unsaturated (including benzo) ketones and which reflect a strengthened n→π^*-transition. By a noteworthy coincidence, the sequiterpenes parasantonide (II) and santonide (III) also feature extraordinarily intense carbonyl absorption[5] and Cotton effect curves[5] whose amplitudes are orders of magnitude greater than those of other carbonyl compounds.[6] The similarity between the optical properties of I and II (or III) is compounded by two observations: first, that the fine-structure in the Cotton effect curve of II is solvent dependent (Fig. 1) in a similar way to that of I,[4] and, second, that the carbonyl bands in the absorption spectrum of II (Table I) feature the same intense (for ketones) quadruplet (in isoöctane) near 288, 297, 307 and 317 mμ which has already been recognized as characteristic of the strengthened n → π^*-transition in β,γ-benzoketones.[4] These intense bands are also exhibited (Table I) by the prototypes bicyclo[2.2.2]oct-5-ene-2-one (IV)[7,8] and bicyclo[2.2.1]hept-5-ene-2-one (V).[7-9]


I


II R = CH$_3$, R′ = H
III R = H, R′ = CH$_3$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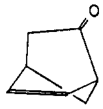
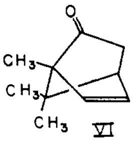
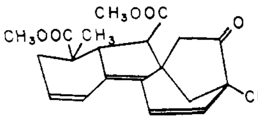
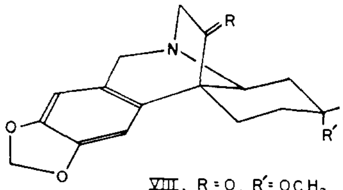

V



VI


VII


VIII, R = O, R′ = OCH$_3$
IX, R = O, R′ = H
X, R = H$_2$, R′ = H

It thus seems inescapable that the virtually identically strengthened O.R.D. curves of β,γ-unsaturated ketones I and II (Fig. 2) are a consequence of the same strengthened n → π^*-transition, even though the compounds owe their dissymmetry to entirely different structural features.

TABLE I

CARBONYL BAND[a] OF SOME β,γ-UNSATURATED KETONES IN ISOÖCTANE

II[b]	286 (562)	*296* (772)	*308* (805)	318 (474)
IV[c]	287.5 (100)	*296* (122)	*306* (113)	317 (60)
V[c]	287.5 (162)	*296.5* (242)	*307.5* (277)	*319.5* (177)
XVIII[d]	286.5 (195)	*296* (253)	*306* (253)	*318* (145)
XIX[d]	290 (228)	*301* (377)	*311* (485)	*324* (334)

[a] Wave length in mμ, maxima italicized. [b] $\lambda_{\max}^{\mathrm{EtOH}}$ 298 mμ (ϵ 1070). [c] *Cf.* ref. 7. [d] Kindly supplied in pure condition (gas-phase chromatography) by Dr. P. R. Story, Bell Laboratories.

Woodward and Kovach[10] have previously pointed out that the high optical rotation and the intense carbonyl absorption of II may have a common basis, and Cookson and Waryiar[11] have suggested

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(1) Preliminary communications: K. Mislow and C. Djerassi, *J. Am. Chem. Soc.*, **82**, 5247 (1960); K. Mislow, M. A. W. Glass, A. Moscowitz and C. Djerassi, *ibid.*, **83**, 2771 (1961).

(2) We gratefully acknowledge financial support by the Alfred P. Sloan Foundation (K. M.) and by National Science Foundation grants No. G-6579 (C. D.) and No. G-15746 (K. M.).

(3) Paper LXVI in the series "Optical Rotatory Dispersion Studies" by C. D.

(4) K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg, J. Weiss and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 1455 (1962); *cf.* K. Mislow, M. A. W. Glass, R. E. O'Brien, P. Rutkin, D. H. Steinberg and C. Djerassi, *ibid.*, **82**, 4740 (1960), for a preliminary report.

(5) S. Mitchell and K. Schwarzwald, *J. Chem. Soc.*, 889 (1939).

(6) *Cf.*, *e.g.*, the tabulations by W. Klyne in "Advances in Organic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, Vol. I, p. 239 ff.

(7) H. Labhart and G. Wagnière, *Helv. Chim. Acta*, **42**, 2219 (1959).

(8) The information in Table I was obtained in our laboratories on gas chromatographically pure material (J. G. Berger).

(9) P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956), report $\lambda\lambda_{\max}^{\mathrm{isooct}}$ 308 mμ (ϵ 266), 297 mμ, 320 mμ.

(10) R. B. Woodward and E. G. Kovach, *ibid.*, **72**, 1009 (1950).

(11) R. C. Cookson and N. S. Waryiar, *J. Chem. Soc.*, 2302 (1956).

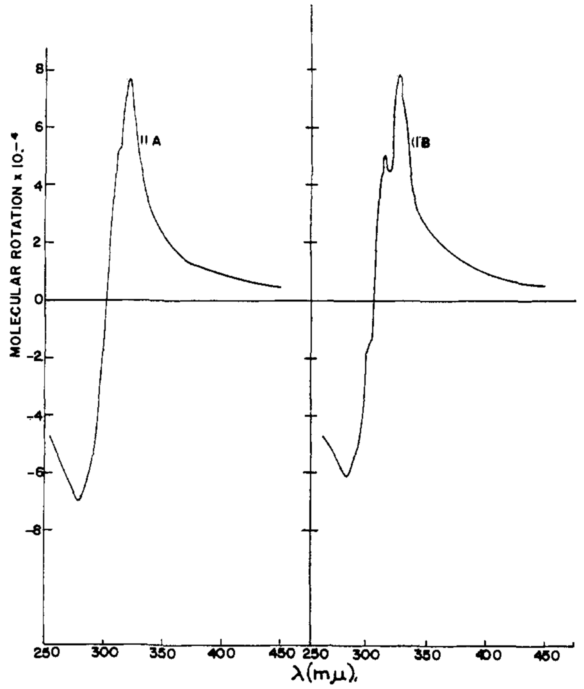

Fig. 1.—Rotatory dispersion curves of parasantonide (II) in ethanol (A) and in isoöctane (B).

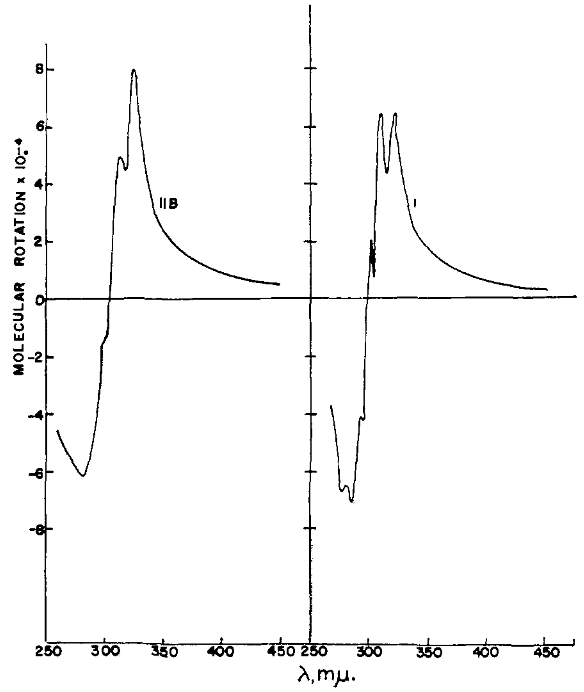

Fig. 2.—Rotatory dispersion curves (isoöctane) of parasantonide (II) and of dimethyldibenzsuberone (I).

that this may be a joint feature of some other β,γ-unsaturated ketones. We shall demonstrate that this proposed duality may be given a basis in theory.

The identity of *sign* of the Cotton effect curves in Fig. 2 is taken as a reflection of the identical relative asymmetric disposition of double bond (inclusive of benzene) and carbonyl groups. The absolute configuration of II being assured,[12] the present correlation establishes the absolute configuration of I, completely independently of and in harmony with the earlier reached absolute configurational assignment.[4]

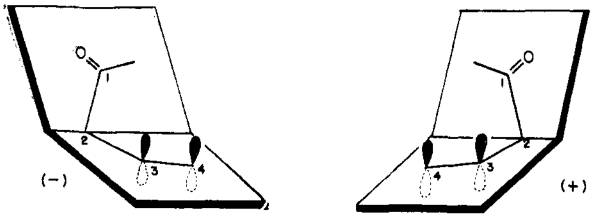

Fig. 3.—Enantiomeric chromophores associated with dissymmetric β,γ-unsaturated ketones.

It is convenient to discuss the chirality of this combined grouping, as found in I and II, in terms of the geometric construct of Fig. 3. Two planes are defined by OC_1C_2 and by $C_2C_3C_4$ which intersect at a dihedral angle of greater than 90° (*ca.* 120° in rigid structures). As indicated in Fig. 3, the arrangement of $O{=}C_1{-}C_2{-}C_3{=}C_4$ assumes one of two enantiomeric conformations, one giving rise to a negative and the other to a positive Cotton effect. Since I and II (stereoformulas) give positive Cotton effects, the absolute configurations of the enantiomeric chromophores in Fig. 3 must correspond to the indicated signs of the respective Cotton effects.

On the basis of the schematic representations in Fig. 3 it may now be conjectured that IV and V (stereoformulas) have intense positive Cotton effects; calculations (below) support this prediction. In the same vein, the recorded[13] negative rotation ($[\alpha]^{20}_{D}$ −735° (alc.)) of dehydrocamphor (VI), whose absolute configuration (stereoformula) follows from its hydrogenation[13] to (+)-camphor,[14] is about as great as that of I and II at the sodium D-line, thus indicating that its O.R.D. curve, as predicted from Fig. 3, would be characterized by a powerful *negative* Cotton effect. This is contrasted with the positive Cotton effect of (+)-camphor[15]; we shall return to a rationalization of this inversion of the Cotton effect below.

The gibberellic acid derivative VII,[16] whose absolute configuration[17] is given in the stereoformula,

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(12) R. B. Woodward, F. J. Brutschy and H. Baer, *J. Am. Chem. Soc.*, **70**, 4216 (1948); R. B. Woodward and P. Yates, *Chemistry & Industry*, 1391 (1954). These authors correlated II[10] and α-santonin, whose absolute configuration was in turn established by chemical correlation with glyceraldehyde by H. Bruderer, D. Arigoni and O. Jeger, *Helv. Chim. Acta*, **39**, 858 (1956), and through rotatory dispersion means by C. Djerassi, R. Riniker and B. Riniker, *J. Am. Chem. Soc.*, **78**, 6362 (1956). The stereochemical integrity of the quaternary atom (C-10 in α-santonin) is maintained throughout these transformations.

(13) Y. Asahina, M. Ishidate and T. Tukamoto, *Ber.*, **69**, 355 (1936).

(14) The absolute configuration of (+)-camphor has been unequivocally established by K. Freudenberg, W. Lwowski and W. Hohmann, *Ann.*, **594**, 76 (1955).

(15) W. Kuhn and H. K. Gore, *Z. physik. Chem.*, **B12**, 389 (1931); C. Djerassi, J. Osiecki, R. Riniker and B. Riniker, *J. Am. Chem. Soc.*, **80**, 1216 (1958).

(16) B. E. Cross, J. F. Grove and A. Morrison, *J. Chem. Soc.*, 2498 (1961).

(17) From the absolute configuration of the cogeneric gibberic and epigibberic acids (G. Stork and H. Newman, *J. Am. Chem. Soc.*, **81**, 3168 (1959); J. F. Grove, J. MacMillan, T. P. C. Mulholland and W. B. Turner, *J. Chem. Soc.*, 3049 (1960)), which in turn are based on O.R.D. arguments (see C. Djerassi "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 137).

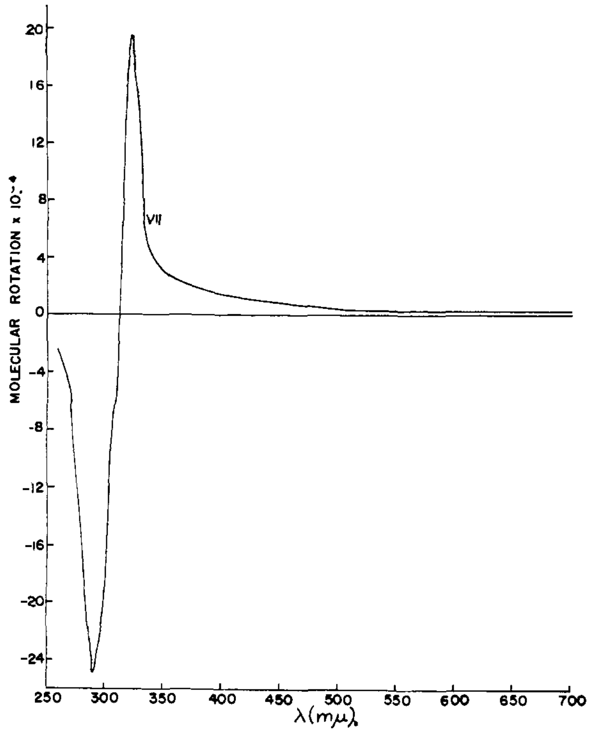

Fig. 4.—Rotatory dispersion curve (dioxane) of gibberellic acid derivative VII.

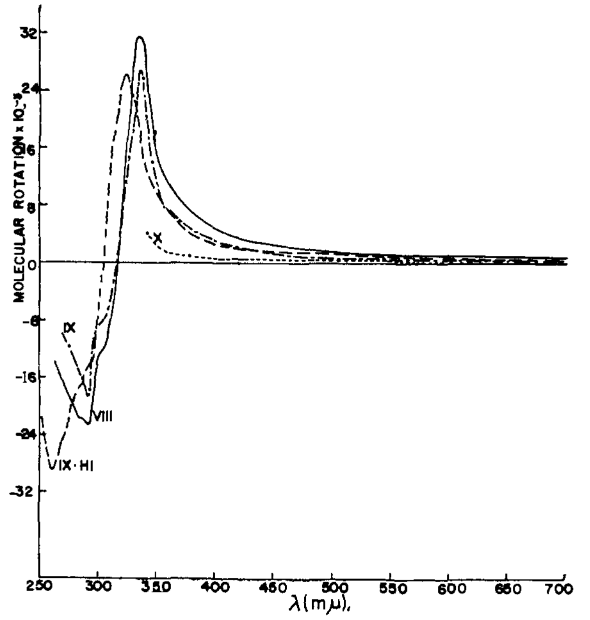

Fig. 5.—Rotatory dispersion curves of oxodihydrohaemanthamine (VIII, dioxane), oxodihydrodemethoxyhaemanthamine (IX, dioxane), hydriodide of IX (water) and crinane (X, chloroform).

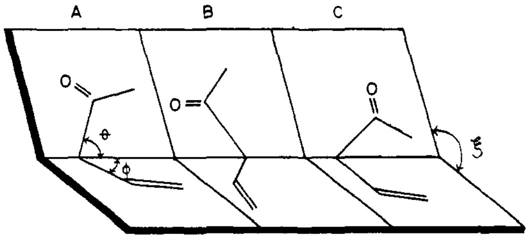

Fig. 6.—Various geometries associated with dissymmetric β,γ-unsaturated ketones.

similarly has an unusually high optical rotation at the D-line ($[\alpha]^{19}\text{D}$ +762° (acetone)).[16] Its high-amplitude positive Cotton effect curve (Fig. 4) may arise from the carbonyl–double bond type of interaction under discussion, although a contribution from a possible asymmetry of the triene chromophore cannot be excluded. Its sign is correctly represented by the absolute configuration of the essential chromophoric system in Fig. 3.

Oxodihydrohaemanthamine (VIII)[18] and oxodihydrodemethoxyhaemanthamine (IX),[19] whose absolute configurations are represented by the stereoformulas,[20] show virtually identical positive Cotton effect curves (Fig. 5). Assuming that the intense long-wave length inflections in the absorption spectrum reflect a strengthened $n \rightarrow \pi^*$-transition,[18,19] the sign of these curves again accords with the absolute configuration of the essential chromophore (Fig. 3). We note that the methylenedioxyphenyl chromophore ($\lambda_{\max}$ *ca.* 295 mμ) cannot be responsible for the observed Cotton curve, since the parent compound (+)-crinane (X) merely exhibits a plain positive curve (Fig. 5), nor can the nitrogen atom be implicated, since the O.R.D. curve of the hydriodide of IX (Fig. 5) does not substantially differ from that of IX itself.

Verbenalin (XI)[21] and chrysanthenone (XII)[22] are reported to have the intensified carbonyl absorption ($\lambda_{\max}^{\text{EtOH}}$ 290 mμ (ε *ca.* 100)) which characterizes the β,γ-unsaturated ketone system under discussion, but the geometries of the corresponding carbonyl–double bond system can no longer be adequately represented by Fig. 3. Of immediate pertinence are the situations represented in Figs. 6A, B and C. Figure 6A covers the cases I–IX already discussed with reference to Fig. 3 and corresponds to a negative Cotton effect curve. Figure 6B is a reasonable representation of the geometry of the corresponding β,γ-unsaturated ketone system in XI, including absolute configuration,[21] and Fig. 6C that of the enantiomer[22] of XII. Disregarding the complication arising from the possible conformational equilibrium in XI,[23] it is remarkable that the Cotton effects (Fig. 7) in XI and XII possess amplitudes which (as in XI) are extraordinarily small or which (as in XII) compare more with those found for ordinary cyclohexanones than those possessed by the constitutionally related ketones previously discussed. Re-examination of

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[18] H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **82**, 197 (1960).

[19] H. M. Fales and W. C. Wildman, *J. Org. Chem.*, **26**, 1617 (1961).

[20] H. M. Fales and W. C. Wildman, *J. Am. Chem. Soc.*, **82**, 3368 (1960); P. W. Jeffs, F. L. Warren and W. G. Wright, *J. Chem. Soc.*, 1090 (1960).

[21] G. Büchi and R. E. Manning, *Tetrahedron Letters*, **No. 26**, 5 (1960).

[22] J. J. Hurst and G. H. Whitham, *Proc. Chem. Soc.*, 160 (1959); *J. Chem. Soc.*, 2864 (1960).

[23] See stereoformula XI in the present paper as well as Ia–Ib in C. Djerassi, T. Nakano, A. N. James, L. H. Zalkow, E. J. Eisenbraun and J. N. Shoolery, *J. Org. Chem.*, **26**, 1192 (1961), for the related terpenoid genipin.

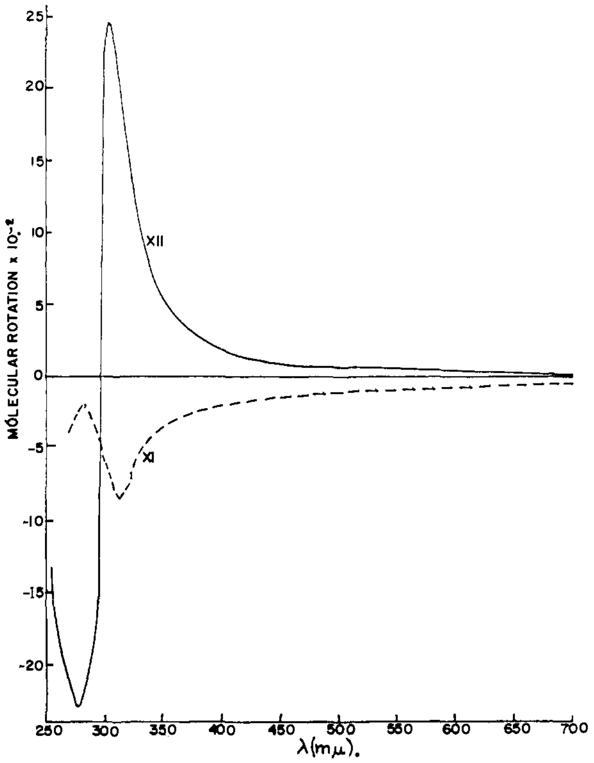
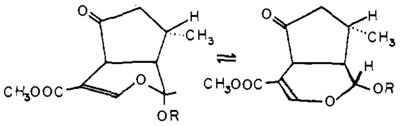
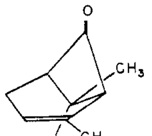


Fig. 7.—Rotatory dispersion curves of verbenalin (XI, water) and chrysanthenone (XII, isoöctane).

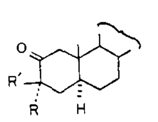
the absorption spectra of XI and XII reveals that the intensity of the band at 290 mμ may be to a considerable extent a result of overlap from an intense band at 238 mμ, probably in part (the —O—C=C—CO— grouping in XI strongly absorbs in this region[21]) the π→π*-transition described by Winstein, *et al.*,[24] for related unsaturated ketones.



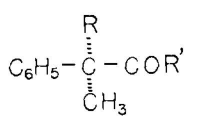
XI, R = β-D-glucose



XII



XIII R = C_6H_5, R' = H
XIV R = H, R' = C_6H_6



$$C_6H_5-\overset{R}{\underset{CH_3}{C}}-COR'$$

(S)-XV R = H, R' = CH_3
(R)-XVI R = C_2H_5, R' = CH_3
(R)-XVII R = C_2H_5, R' = C_2H_5

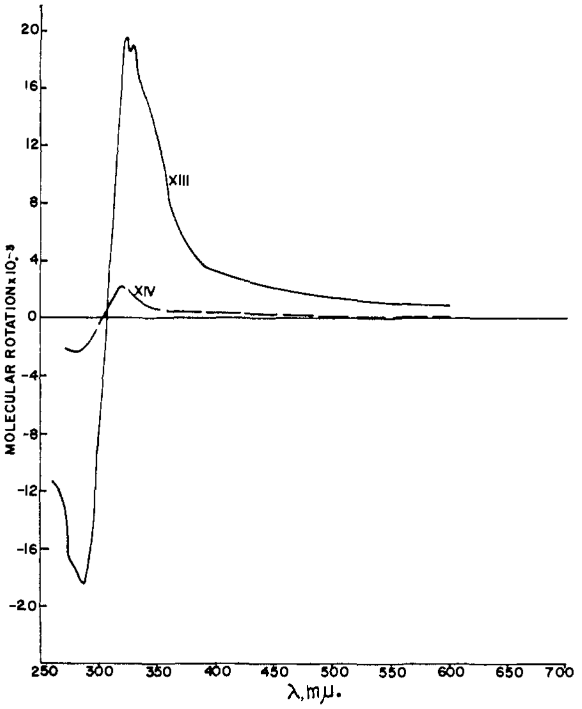


Fig. 8.—Rotatory dispersion curves of 3α-phenylcholestan-2-one (XIII, methanol) and the 3β-isomer (XIV, dioxane).

For compound XI we believe this to be the case, although for compound XII we feel that the observed enhanced value for ϵ_{max} is significant and not merely an artifact caused by overlapping absorption bands.

We conclude that the amplitude of the Cotton effect curves in β,γ-unsaturated ketones is critically dependent on the relative disposition of carbonyl group and double bond, and that the high amplitudes which we have considered characteristic of such structures are typical of (although not necessarily confined to) conformations approximating the array in Fig. 3 (or Fig. 6A). This conclusion, which has support in theoretical considerations (as will be shown below), *sometimes permits the assignment of rotomeric conformations to β,γ-unsaturated ketones in situations where free rotation may occur.*

Thus, in the 3-phenylcholestan-2-ones,[25] the tremendous positive Cotton effect (Fig. 8) of the axial 3α-isomer XIII, which is accompanied by the typically intense absorption in the carbonyl region, suggests the prevalence of conformations in which the orientation of the π-electrons of the benzene ring relative to electrons of the carbonyl group is geometrically favorable for enhancement. The *sign* of the curve is in harmony with the construct in Fig. 3 for the absolute configuration shown. By contrast, the equatorial 3β-isomer XIV, in which such orientations are not possible, has the expected normal absorption spectrum and O.R.D. amplitude (Fig. 8).

Subject to an additional assumption, the conformational analysis may be extended to the open-chain α-phenyl ketones. Of the conformations

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[24] S. Winstein, L. de Vries and R. Orloski, *J. Am. Chem. Soc.*, **83**, 2020 (1961).

[25] R. C. Cookson and J. Hudec, *Proc. Chem. Soc.*, 24 (1957).

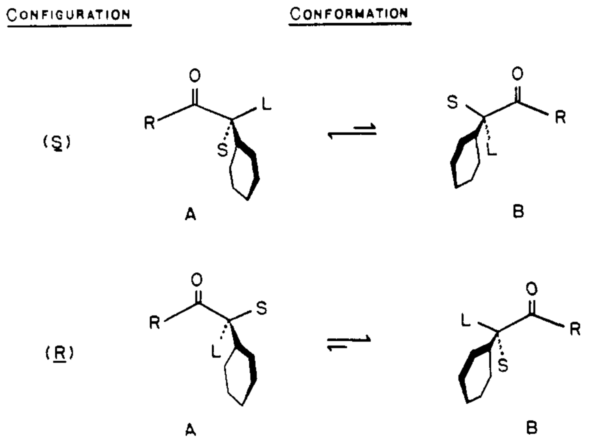

Fig. 9.—Conformational equilibria in acyclic α-phenylketones. A and B are diastereomeric conformers associated with enantiomeric Cotton effects.

which may exist for such ketones, only those will be of interest for the purpose of the present discussion in which the phenyl and carbonyl groups have the proper orientation for high optical activity. These will, of course, include those conformers approximating the array in Fig. 3. Somewhat arbitrarily we shall confine our considerations *solely* to such conformers and take the contributions of all others as relatively unimportant; detailed considerations become awkward because of the extremely large range of possible conformers. However, in the Discussion section below, we shall cite three criteria which justify the disregard of a great many of the conformers.

With the assumption just stated, the resulting simplified equilibrium is depicted in Fig. 9. For each enantiomer ((*R*)) and ((*S*)) two pertinent disastereomeric conformations exist, one (A) corresponding to a positive, the other (B) to a negative Cotton effect (*cf.* Fig. 3). In the (*S*)-A conformation, the smaller (S) group on the asymmetric carbon is in a less favorable steric position (compression against R and against the phenyl *ortho*-hydrogen) than the larger (L) group, whereas in (*S*)-B it is the larger group which occupies the unfavorable site. Since compression of L is energetically more costly than compression of S, the A-conformation will predominate in the equilibrium. By the same token, (*R*)-B will predominate in the enantiomeric equilibrium, and to the identical extent. It follows that the (*S*)-isomer has a net positive and the (*R*)-isomer a net negative Cotton curve. The *net* amplitude is a function of the relative difference in size of L and S: the larger the relative difference, the greater the deviation of A/B from unity and the more pronounced the *net* Cotton effect.

Application of these concepts serves to clarify a number of previously unexplained observations. Thus, the sign of the (positive) Cotton effect curves[26] of (*S*)-XV[27] and related (*S*)-3-aryl-2-alkanones, as well as the sign of the Cotton effect (Fig. 10) of (*R*)-XVI[28] (negative) and of (*S*)-XVII[28] (positive) agree with our analysis. Furthermore, since the relative difference in size of alkyl and hydrogen is much greater than the relative difference in size of methyl and ethyl groups, we would expect the amplitudes of the Cotton effect curves in XV and related 3-aryl-2-alkanones to be considerably greater than that in XVI or XVII. This expectation is borne out by the observation that the peak heights in XV and XVI (or XVII) are 37,500°[26] and 2,700° (Fig. 10), respectively. It has been pointed out[29] that a wide variety of acyclic ketones (+)-(*S*)-RCH-$(C_6H_5)COR'$ have rotations which are significantly larger in the visible than those of the branched analogs (*e.g.*, XVI), even though the absorption spectra are virtually superimposable. The key function of the grouping $-CH(C_6H_5)CO-$ can now be understood in terms of the large relative difference in size of alkyl and hydrogen which leads to a reasonably large A/B ratio and a pronounced *net* Cotton effect, as reflected by the high rotation in the visible region.

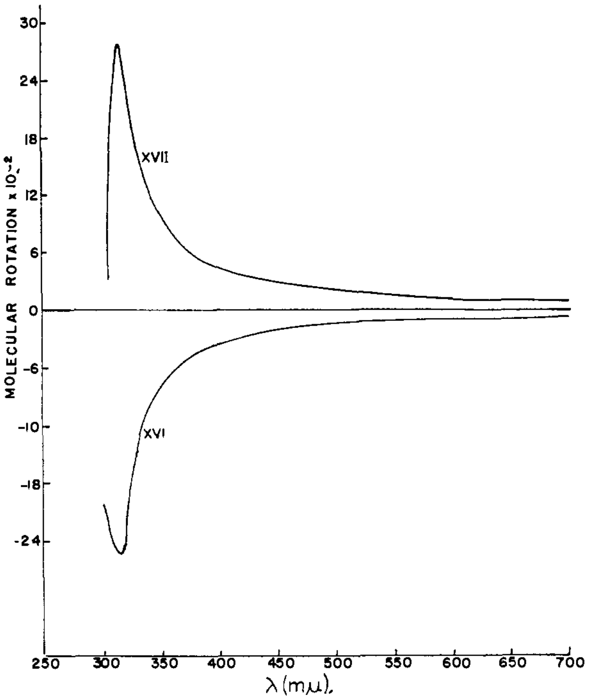

Fig. 10.—Rotatory dispersion curves (dioxane) of 3-methyl-3-phenyl-2-pentanone (XVI) and 4-methyl-4-phenyl-3-hexanone (XVII).

Experimental[30]

Parasantonide (II) (R. B. Woodward), R.D. (IIA in Fig. 1) in ethanol (*c* 0.01): $[\alpha]_{589}$ +772°, $[\alpha]_{322.5}$ +31000°, $[\alpha]_{280}$ −28800°, $[\alpha]_{255}$ −18850°; R.D. (IIB in Fig. 1) in isoöctane (*c* 0.012): $[\alpha]_{589}$ +999°, $[\alpha]_{325}$ +32500°, $[\alpha]_{317.5}$ +18150°, $[\alpha]_{312.5}$ +20450°, $[\alpha]_{300}$ −6250° (sh.), $[\alpha]_{282.5}$ −25350°, $[\alpha]_{260}$ −18400°; for ultraviolet data, see Table I.

Methyl 1,7-dimethyl-8-oxo-7α-10α-gibba-3,4a(4b),5-triene-1,10-dicarboxylate (VII) (J. F. Grove), R.D. (Fig.

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[26] B. Sjöberg, *Arkiv Kemi*, **15**, 473 (1960).

[27] Absolute configuration: K. Mislow and J. Brenner, *J. Am. Chem. Soc.*, **75**, 2318 (1953).

[28] D. J. Cram and J. D. Knight, *ibid.*, **74**, 5835 (1952); absolute configuration: D. J. Cram and J. Allinger, *ibid.*, **76**, 4516 (1954).

[29] K. Mislow and C. L. Hamermesh, *ibid.*, **77**, 1590 (1955).

[30] We are greatly indebted to the investigators listed for donating samples and to Mrs. Ruth Records for the rotatory dispersion curves, determined on a Rudolph recording spectropolarimeter.

4) in dioxane (c 0.10 to 400 mμ, then 0.0008): $[\alpha]_{589}$ +840°, $[\alpha]_{322}$ +55000°, $[\alpha]_{292}$ −70000°, $[\alpha]_{260}$ −6870°; $\lambda\lambda^{\text{diox}}$ 250 mμ (log ϵ 3.94), 262 mμ (log ϵ 4.10), 276 mμ (log ϵ 4.25), *286* mμ (log ϵ 4.33), 305 mμ (log ϵ 4.17), *310* mμ (log ϵ 4.16), 316 mμ (log ϵ 4.13).

Oxodihydrohaemanthamine (**VIII**) (W. C. Wildman), R.D. (Fig. 5) in dioxane (c 0.012 to 330 mμ, then 0.006): $[\alpha]_{589}$ +386°, $[\alpha]_{335}$ +10500°, $[\alpha]_{292}$ −7640°, $[\alpha]_{265}$ −4650°; $\lambda\lambda^{\text{diox}}$ *215* mμ (log ϵ 3.80), 290 mμ (log ϵ 3.21), *296* mμ (log ϵ 3.33), 317 mμ (log ϵ 2.98), 330 mμ (log ϵ 2.76).

Oxodihydrodemethoxyhaemanthamine (**IX**) (W. C. Wildman), R.D. (Fig. 5) in dioxane (c 0.14 to 340 mμ, then 0.004): $[\alpha]_{589}$ +230°, $[\alpha]_{337.5}$ +9780°, $[\alpha]_{305}$ −3250° (infl.), $[\alpha]_{292}$ −6940°, $[\alpha]_{270}$ −3690°; $\lambda\lambda^{\text{diox}}$ *208* mμ (log ϵ 4.44), *245* mμ (log ϵ 3.71), 288 mμ (log ϵ 3.65), *295* mμ (log ϵ 3.75), 315 mμ (log ϵ 3.45), 330 mμ (log ϵ 3.25).

Oxodihydrodemethoxyhaemanthamine hydriodide (W. C. Wildman), R.D. (**IX-HI** in Fig. 5) in water (c 0.02 to 320 mμ, then 0.004): $[\alpha]_{589}$ +131°, $[\alpha]_{315}$ +6500°, $[\alpha]_{262}$ −7310°, $[\alpha]_{25}$ −4535°; $\lambda\lambda^{\text{water}}$ *220* mμ (log ϵ 4.34), *255* mμ (log ϵ 3.81), 280 mμ (log ϵ 3.70), 292 mμ (log ϵ 3.68), 305 mμ (log ϵ 3.52).

(+)-Crinane (**X**): R.D. (Fig. 5) in chloroform, enantiomeric to the experimentally determined curve for (−)-crinane.[20]

Verbenalin (**XI**) (G. Büchi), R.D. (Fig. 7) in water (c 0.105): $[\alpha]_{589}$ −17°, $[\alpha]_{313}$ −217°, $[\alpha]_{283}$ −55°, $[\alpha]_{270}$ −128°; $\lambda\lambda_{\text{max}}^{\text{water}}$ 238 mμ (ϵ 11,100), infl. 290 mμ (ϵ 186).

Chrysanthenone (**XII**) (G. H. Whitham), R.D. (Fig. 7) in isoöctane (c 0.6): $[\alpha]_{589}$ +25°, $[\alpha]_{312}$ +1640°, $[\alpha]_{278}$ −1540°, $[\alpha]_{255}$ −890°; $\lambda\lambda_{\text{max}}^{\text{isooct}}$ 238 mμ (ϵ 870), 290 mμ (ϵ 118).

3α-Phenylcholestan-2-one (**XIII**) (R. C. Cookson), R.D. (Fig. 8) in methanol (c 0.05): $[\alpha]_{589}$ +180°, $[\alpha]_{322}$ +4210°, $[\alpha]_{287}$ −3870°, $[\alpha]_{260}$ −2430°; $\lambda_{\text{max}}^{\text{MeOH}}$ 295 mμ (ϵ 231).

3β-Phenylcholestan-2-one (**XIV**) (R. C. Cookson), R.D. (Fig. 8) in dioxane (c 0.10): $[\alpha]_{589}$ +16°, $[\alpha]_{318}$ +488°, $[\alpha]_{279}$ −492°, $[\alpha]_{270}$ −456°; $\lambda_{\text{max}}^{\text{diox}}$ 287 mμ (ϵ 74).

3-Methyl-3-phenyl-2-pentanone (**XVI**) (D. J. Cram), R.D. (Fig. 10) in dioxane (c 0.15): $[\alpha]_{589}$ −60°, $[\alpha]_{317}$ −1480°, $[\alpha]_{300}$ −1145°.

4-Methyl-4-phenyl-3-hexanone (**XVII**) (D. J. Cram), R.D. (Fig. 10) in dioxane (c 0.16): $[\alpha]_{589}$ +55°, $[\alpha]_{315}$ +1500°, $[\alpha]_{305}$ +180°.

Discussion

Symmetric and Dissymmetric Chromophores.—All optically active chromophores must be nonsuperimposable on their mirror images and are perforce dissymmetric. When this dissymmetry is an inherent property of the molecule, as for example in hexahelicene,[31] it is convenient to speak of an *inherently dissymmetric chromophore*. For reasons discussed elsewhere,[32] such chromophores may be characterized by the absence of any extremely weak absorption bands ($\epsilon_{\text{max}} <$ 100) and the presence of relatively high molecular amplitudes of the rotatory dispersion curve, corresponding to reduced rotational strengths of approximately 25 or greater. In fact, unusually high amplitudes may be taken as *prima facie* evidence for the presence of a dissymmetric chromophore. Such chromophores are to be contrasted with *asymmetrically perturbed, symmetric chromophores*, *e.g.*, the carbonyl group in 3-methylcyclohexanone, where asymmetry has been induced by the vicinal action of the asymmetric molecular environment on the inherently symmetric carbonyl group.

It must be stressed, however, that the above classification is solely an expedient for elucidating the optical properties of a chromophore. The designation of an optically active chromophore as inherently dissymmetric or inherently symmetric, but asymmetrically perturbed, is a matter of convenience for the investigator, since from a theoretical point of view either outlook must ultimately lead to the same result.

Extension of the Octant Rule.—The original statement of the octant rule[33] rested on theoretical considerations that were shaped by the perturbed symmetric chromophore point of view. Subsequent investigations have borne out the merit of this approach for perturbing hydrogen and alkyl groups.[34] The body of experimental evidence presented in the first part of this paper indicates that the long-wave length carbonyl transition in the compounds considered has taken on, relatively speaking, some of the aspects usually characteristic of the transitions of dissymmetric chromophores, *i.e.*, intense absorption and strong Cotton effects. This leads us to broaden the original statement of the octant rule in order to encompass the peculiar effect of π-systems of the type discussed earlier. *We may now state that there exist substituents whose geometric disposition in a particular far octant is sufficient for the determination of the sign of the long-wave length Cotton effect.* The presence of such a substituent, when suitably oriented, overrides all other considerations that might arise with regard to the contributions of any weakly perturbing groups such as alkyls and hydrogens. Hence, by focusing attention solely on the important substituent group, a ready determination of absolute configuration is possible. Conversely, conformations may often be assigned if the absolute configuration is known.

In the present paper we are concerned mainly with β,γ-unsaturated ketones where the important substituent groups are double bonds, aromatic moieties and related π-systems. However, it will be noted that the earlier enunciated α-haloketone rule[35] satisfies the same criteria in terms of stereochemical applicability, *i.e.*, the sign of the Cotton effect can usually be derived merely by locating the octant containing the axial halogen atom and ignoring[36] other substituents such as alkyl groups. Within the framework of the present empirical discussion, we could regard α-haloketones as occupying a position intermediate between that of the dissymmetric chromophore, characteristic of the β,γ-unsaturated ketones, and the perturbed symmetric chromophore of the alkyl cyclohexanones.

Before proceeding, we may now note that the present statement of the octant rule has no difficulty reconciling such apparent anomalies as the different signs for the long-wave length Cotton effect evinced by (+)-camphor and its dehydro derivative VI as discussed in the earlier part of this article.

Relevant Molecular Orbitals.—The lowest electronic transition in an isolated carbonyl group can

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

[32] A. Moscowitz, Chap. 12 of C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

[33] W. Moffitt, R. B. Woodward, A. Moscowitz, W. Klyne and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961).

[34] L. C. Snyder and A. Moscowitz, unpublished calculations quoted by A. Moscowitz, *Tetrahedron*, **13**, 48 (1961).

[35] C. Djerassi and W. Klyne, *J. Am. Chem. Soc.*, **79**, 1506 (1957); C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, pp. 120–129.

[36] See C. Djerassi, *Tetrahedron*, **13**, 24 (1961).

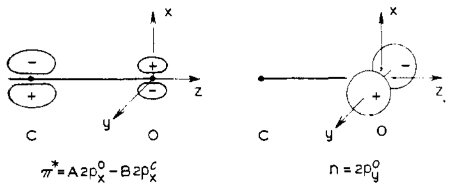

Fig. 11.—Schematic representation of orbitals involved in the n → π*-transition of an isolated carbonyl chromophore.

be considered as an n → π*-transition roughly involving the promotion of an electron from a nonbonding $2p_y$ orbital situated on the oxygen atom to an antibonding π-type orbital involving $2p_x$ orbitals of both the carbon and the oxygen atoms.[37] The orbitals are indicated schematically in Fig. 11, as are our designations for them. On symmetry grounds the transition is electric dipole forbidden (electric dipole transition moment $\vec{\mu}_e = 0$) but magnetic dipole allowed (magnetic dipole transition moment $\vec{\mu}_m \neq 0$). Since the magnitude of the rotational strength depends upon the scalar product $\vec{\mu}_e \cdot \vec{\mu}_m$[38] of these vector quantities, the transition will be optically inactive unless the orbitals of the C═O group are perturbed in such a way as to produce a non-zero component of $\vec{\mu}_e$ along the direction of $\vec{\mu}_m$. As we have already noted, in 3-methylcyclohexanone this effect is brought about by the asymmetrically disposed substituents.

An ethylenic group also contains a π-system. If such a functionality is situated in the vicinity of a C═O group, the over-all effect will be the creation of an extended π-system that utilizes the π-orbitals of both components and which is diene-like in conception. The open-chain, α,β-unsaturated ketones provide an obvious example, but it should be emphasized that direct chemical bonding in the classical sense is not essential for the existence of the composite chromophore. In such chromophores, the long-wave length transition is still n → π*, but the π*-orbital is now the first antibonding orbital of the extended π-system.

In the case of the α,β-unsaturated ketones the most probable conformation is the one in which the component 2p-atomic orbitals of the π-system are all directed along the *x*-axis and perpendicular to the C═C—C═O plane, as indicated in Fig. 12. Although the symmetry of the situation has been reduced from that in, say, formaldehyde, where there are two orthogonal symmetry planes, the reduction is of small consequence for the intensity of the n→π*-transition.[37] Of course, intense transitions of the π → π*-type, such as occur in butadiene are possible (*e.g.*, the 210 mμ transition of acrolein) as indeed they were in formaldehyde (*e.g.*, the 155 mμ transition).

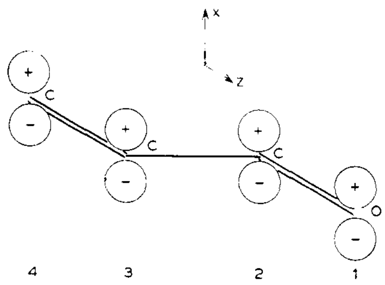

Fig. 12.—Schematic representation of the π-system in α,β-unsaturated ketones.

As Labhart and Wagnière[7] point out, the situation is severely altered when the bond containing the p-orbitals labeled 3 and 4 (Fig. 12) is twisted with respect to the double bond 1–2. There will, in general, still be an extended π-system, but that π-system can now overlap the $2p_y{}^0$ non-bonding orbital. The classification of orbitals into n and π no longer holds in the strictest sense, for the effect is to mix some π character in with the nonbonding orbital n, so that it is now more accurately described as

$$n = 2p_y{}^{\circ} + \lambda\pi \qquad (1)$$

where π indicates a molecular orbital that is some linear combination of the four basic 2p-atomic orbitals of the system.[39] The effect of this small amount of admixed π-character is to cause the erstwhile n→π*-transition to take on (approximately to the extent λ) the aspects of an allowed π→π*-transition; $\vec{\mu}_e$ will no longer be zero and there will be a concomitant increase in intensity.

The rotational strength, which governs the sign and magnitude of the Cotton effect associated with the transition, is proportional to the component of $\vec{\mu}_e$ in the direction of $\vec{\mu}_m$. Hence, in general, the enhanced intensity will be accompanied by an enhanced Cotton effect. This is nicely demonstrated in the case of dimethyldibenzsuberone (I) where, because symmetry considerations require that $\vec{\mu}_e$ and $\vec{\mu}_m$ be parallel for the long-wave length transition, one has all the information necessary to calculate the rotatory dispersion curve from the absorption curve, provided that the following assumptions are made:

(1) The carbonyl partial absorption band, 3 in Fig. 13, may be obtained by subtracting the dotted tail 2 from the experimental curve 1. This dotted tail represents our approximation of the adjacent (aromatic) absorption band which extends into the region of our interest.

(2) The value of $\vec{\mu}_e$ can be obtained from the

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[37] H. L. McMurry and R. S. Mulliken, *Proc. Natl. Acad. Sci. U. S.*, **26**, 312 (1940); H. L. McMurry, *J. Chem. Phys.*, **9**, 231 (1941); J. W. Sidman, *ibid.*, **27**, 1270 (1957); J. W. Sidman, *Chem. Revs.*, **58**, 689 (1958).

[38] Strictly speaking, the rotational strength *R* is calculated as the imaginary part of $\vec{\mu}_e \cdot \vec{\mu}_m$. However, if we choose the orbitals to be real, $\vec{\mu}_e$ will be real and $\vec{\mu}_m$ purely imaginary. If we, therefore, use the symbol $\vec{\mu}_m$ to indicate the *imaginary* part of the magnetic part of the magnetic dipole transition moment, we may write simply $R = \vec{\mu}_e \cdot \vec{\mu}_m$. In the present paper, we shall adhere to this practice. It might also be noted that with relative phases of the orbitals fixed as in Fig. 11, $\vec{\mu}_m$ as we have defined it points in the negative *z* direction along the C═O bond.

[39] The designation of a molecular orbital as "π" implies, *inter alia*, that the orbital is antisymmetric with respect to reflection in a particular plane. For a twisted chromophore such as we are describing, such a plane no longer exists. However, we feel that no confusion will arise if we retain the designation for those molecular orbitals that would be strictly π in the planar chromophore.

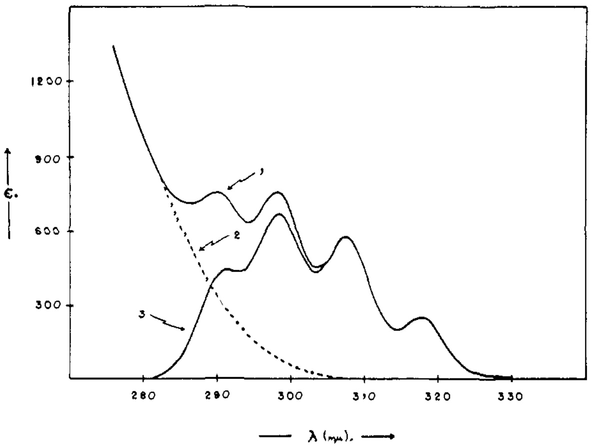

Fig. 13.—Absorption spectrum of dimethyldibenzsuberone (I) before (1) and after (3) subtraction of the biphenyl conjugation band (2).

intensity of the transition associated with the area under curve 3 of Fig. 13.

(3) The magnetic dipole transition moment is roughly equal to that found in saturated ketones (*ca.* one Bohr magneton) and lies along the C=O bond.

(4) Because the transition is now electric dipole allowed in character, the necessary shape factor can be obtained from a Kronig–Kramers transform of the partial absorption band.[32]

(5) The background contribution of the higher lying transitions is small and may be neglected. Granting these premises, then one may calculate the curve shown in Fig. 14, which agrees quite well with experiment. It is particularly important to note that assumption 4 appears to be valid, for it is essential that the transition be electric dipole allowed if one is to make a successful prediction of the rotatory dispersion.

Since the nature of the long-wave length transition in bicyclooctenone (IV) and norbornenone (V) is the same as in dimethyldibenzsuberone (I), the rotatory dispersion curves for these molecules are in principle calculable by the procedure just discussed. However, for bicyclooctenone and norbornenone, symmetry does not require that $\vec{\mu}_e$ and $\vec{\mu}_m$ be collinear as in dissymmetric (but not asymmetric) dimethyldibenzsuberone. Hence, if we wish to make no further assumptions, we can predict only the shape of the rotatory dispersion curve for IV or V, but no scale factor for it. Our predicted shapes are shown in Figs. 15 and 16 along with the pertinent absorption curves.[40]

The Sign of the Rotational Strength R.—In the dimethyldibenzsuberone calculation just described, the magnitude of the electric dipole transition moment was obtained from the experimental absorption curve. However, to obtain $\vec{\mu}_e$ without prior knowledge of the intensity of absorption is a much more difficult matter, for it presupposes

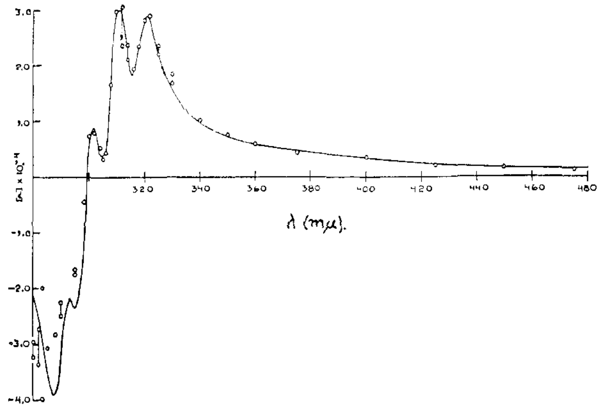

Fig. 14.—Calculated (solid line) and experimental (circles) rotatory dispersion curves (isoöctane) of dimethyldibenzsuberone (I).

the ability to calculate λ of eq. 1 accurately. In their own paper, Labhart and Wagnière[7] invoked reasonable order of magnitude arguments to show in fact that λ took on acceptable values for their mechanism of intensity enhancement. However, since they were concerned with intensities rather than rotational strengths, the sign of λ did not concern them.

We noted that according to the scheme of Labhart and Wagnière the long-wave length transition is in part π→π* in character, roughly to the extent λ. Denoting the portion of the electric dipole transition moment associated with the π→π*-transition as $\vec{\mu}_e^{\pi}$, we may express the rotational strength R as

$$R \approx \lambda \vec{\mu}_e^{\pi} \cdot \vec{\mu}_m \qquad (2)$$

if we allow that $\vec{\mu}_e^{\pi}$ is much greater than any electric dipole transition that might arise through vicinal action of asymmetrically disposed alkyl groups. If further we accept assumption 3 above that $\vec{\mu}_m$ is about the same in all the molecules we are considering, then the sign and magnitude of R are fixed by the signs and magnitudes of λ and the component of $\vec{\mu}_e^{\pi}$ along the direction of $\vec{\mu}_m$. Hence the conditions for the enhanced Cotton effect are that λ and the z-component of $\vec{\mu}_e^{\pi}$ be significant. As we show below, these conditions are met in the majority of compounds we considered earlier, and in fact in such a way as to lead to the broadened statement of the octant rule of the present paper. However, we emphasize the importance of taking cognizance of the relative geometries of the C=O and ethylenic (or other π-) groups.

For example: (1) Using the method of the next section one can show that the verbenalin conformer on the right in XI should show no significant enhancement of either the absorption intensity or the Cotton effect of the 300 mμ transition for the reasonably assumed set of atomic coördinates

	O	C_1	C_4	C_3
x, Å.	0	0	1.26	1.84
y, Å.	0	0	−2.15	−2.90
z, Å.	0	−1.22	−1.64	−2.57

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(40) The curve-analyzing apparatus at the National Institutes of Health, Bethesda, Md., was used to help effect the necessary Kronig–Kramers transforms. We should like to express our appreciation to Drs. Elliot Charney and Joseph Hayes for their generous aid in this connection.

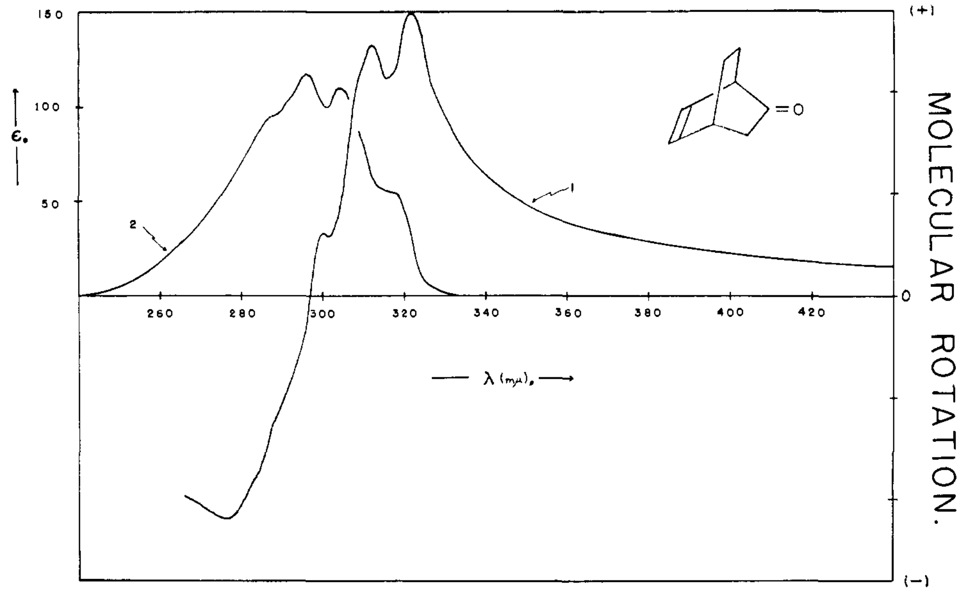

Fig. 15.—Calculated rotatory dispersion curve (1) and experimental absorption curve (2) of bicycloöctenone (IV) in isoöctane. Ordinate on the right (precise scale factor unknown and therefore not indicated) refers to curve 1 and ordinate on the left to curve 2.

One can also show that the conformer on the left in XI should exhibit an enhanced Cotton effect. In view of the experimental evidence cited previously, we feel that the other conformer is dominant.

(2) For chrysanthenone (XII) we would expect enhanced absorption of the n→π*-transition. However, $\vec{\mu}_e^{\pi}$ will be directed principally along the C═C bond which is perpendicular to the C═O bond, the direction of $\vec{\mu}_m$. Hence no marked enhancement of the Cotton effect is to be anticipated.

(3) In the case of the open-chain α-phenyl ketones, many of the conformers make no significant contribution to the optical activity because one or more of the following conditions obtain: (a) The π-systems of the carbonyl and aromatic moieties do not overlap significantly and no extended chromophore is formed. (b) There is no significant overlap of the non-bonding orbital with the extended π-system so that $\lambda \approx 0$. (c) The electric dipole transition moment $\vec{\mu}_e^{\pi}$ is perpendicular or at best makes a very large acute angle with $\vec{\mu}_m$.

Semi-quantitative Considerations.—Our main concern here is with signs and orders of magnitude. Accordingly, we shall be content with an unsophisticated Hückel-type approach but one which we feel adequate for the purpose stated. More quantitative calculations must await further work. Our orbital description will differ in no essential way from that of Labhart and Wagnière,[7] although we shall find it convenient at times to employ a slightly different formalism.

We shall consider first the case of bicyclooctenone. We neglect the effects of overlap, hyperconjugation and molecular environment and take the simple Hückel orbitals for ethylene shown in Fig. 17. Here β_0 is the usual carbon–carbon resonance integral, an inherently negative quantity, which is set equal to 3.25 ev. so as to be roughly in accord with the ethylenic transition in cyclic olefins.[41] The energies of the orbitals are also indicated in Fig. 17, with the carbon coulomb integral α taken as the zero of energy. If one chooses $\beta_{C=O} = 1.2\beta_0$ and the coulomb integral for oxygen equal to $\alpha + 0.7\beta_0$ then for an isolated C═O chromophere one obtains Pople and Sidman's[37] estimated self-consistent field π-orbitals for formaldehyde, and approximately the experimental energy separation of about 8 ev.[42] This energy level scheme is also indicated in Fig. 17.

Suppose now that the π-systems of the C═C and C═O groups are allowed to couple. If one assumes with Labhart and Wagnière that the resonance integral connecting the two π-systems is proportional to the overlap of the nearest neighbor atomic orbitals, one is led to choose a value of about $0.2\beta_0$ for this integral. There results the set of molecular orbitals shown in the lower half of Fig. 17. It will be noticed that the highest filled bonding orbital π_2 is mostly ethylenic in character and that the lowest antibonding orbital π_3 still contains an appreciable portion of the isolated C═O antibonding orbital.

As Labhart and Wagnière recognized, ionization potential data indicate that the bonding ethylenic orbital (and hence π_2) and the non-bonding orbital $2p_y^0$ are very close in energy. They estimate the difference as 0.2 ev. If we take the ionization values quoted in Field and Franklin[43] for ethylene

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[41] S. Stokes and L. W. Pickett, *J. Chem. Phys.*, **23**, 258 (1955); L. W. Pickett, M. Muntz and E. M. McPherson, *J. Am. Chem. Soc.*, **73**, 4862 (1952).

[42] W. C. Price, *J. Chem. Phys.*, **3**, 256 (1935). The analogous transition in acetone is approximately equienergetic; W. A. Noyes, A. B. F. Duncan and W. M. Manning, *J. Chem. Phys.*, **2**, 717 (1934).

[43] F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

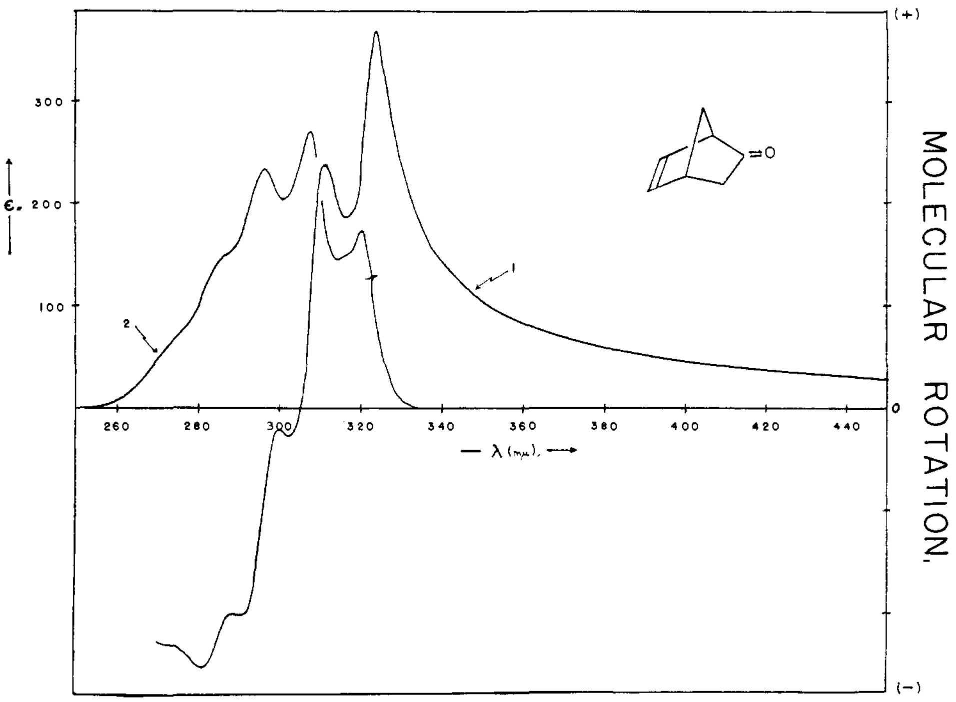

Fig. 16.—Calculated rotatory dispersion curve (1) and experimental absorption curve (2) of norbornenone (V) in isooctane. Ordinate on the right (precise scale factor unknown and therefore not indicated) refers to curve 1 and ordinate on the left to curve 2.

and formaldehyde, we estimate that π_2 is higher than $2p_y{}^0$ by 0.24 ev., or about -0.074β. Therefore, using the proportionality-to-overlap assumption for $\beta_{C=O}$ in conjunction with first-order perturbation theory, we find that the coupling constant λ of eq. 1 is given by

$$\lambda \approx \frac{1.2\beta}{0.074\beta}\bar{S} \approx 16\bar{S}$$

where $\bar{S}$ is the ratio of the overlap of the $2p_y{}^0$ and π_2 orbitals to the overlap of like 2p orbitals of carbon oxygen separated by a distance of 1.22 Å. Hence, λ will be positive or negative as the overlap between $2p_y{}^0$ and π_2 is positive or negative.

For the atomic coördinates assumed for bicyclooctenone by Labhart and Wagnière[7] (enantiomer of IV), the value of $\bar{S}$ is determined almost wholly by the overlap of the $2p_y{}^0$ orbital with the 2p atomic orbital on carbon 3 (Fig. 3). For effective nuclear charges of 3.18 and 4.55 for carbon and oxygen, respectively, $\bar{S} \approx +0.006$ when the ethylene group occupies the upper right-hand far octant. Hence, for this geometry, $\lambda \approx +0.1$. Were the ethylenic group situated in the upper left or lower right-hand far octant, the sign of the overlap and hence the sign of λ would be negative.

The electric dipole transition moment for the long-wave length transition may now be approximated as roughly 0.1 the value of $\vec{\mu}_e$ for the intense $\pi_2 \rightarrow \pi_3$-transition. For reasons discussed elsewhere,[44] we prefer to calculate $\vec{\mu}_e$ in dipole velocity form. If we do so by expanding the molecular orbitals π_2 and π_3 in terms of their atomic orbitals and further assume that we need consider only matrix elements involving nearest neighbor atoms, we calculate a transition moment of 0.3 Debye, which is of the same order of magnitude as the 0.4 Debye value we can obtain from our experimental absorption curve. In addition, and more important, the z-component of $\vec{\mu}_e$ is positive. Since $\vec{\mu}_m$ for the lowest carbonyl transition is negative (*cf.* footnote 40), the sign of the rotational strength R emerges as negative for the enantiomer of IV.

The critical point of this calculation is that the sign of the z-component of $\vec{\mu}_e$ is determined by the relative signs of the coefficients of the atomic orbitals which go to make up the molecular orbitals. Although our estimates of the magnitudes of these coefficients may be in error, our knowledge of their signs is most probably not. In the case of a butadiene-like π-system such as is indicated in the lower half of Fig. 17, the energies of the molecular orbitals will increase with increasing number of nodes, zero nodes for the lowest level to three for the highest antibonding one, to give the relative signs for the coefficients indicated in the figure. For a given geometry these will in turn fix the sign of the overlap at $2p_y{}^0$ with π_2 and hence the sign of λ. Since the sign of R is fixed once the sign of λ and the relative signs of the z-components of $\vec{\mu}_e$ and $\vec{\mu}_m$ are fixed, we see that the mechanism of intensity enhancement advanced by Labhart and Wagnière[7] also fixes the sign of the long-wave length Cotton effects.

For the geometry just considered, which approximates the array of Fig. 3, it may be noted that none of the three criteria mentioned at the end of the preceding section are met. Rather it achieves an adequate compromise in maintaining

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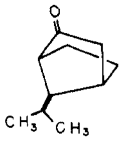
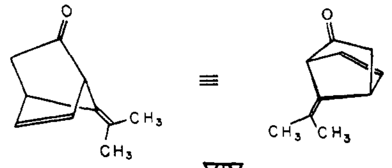
(44) A. Moscowitz, Doctoral Thesis, Harvard University, 1957; W. Moffitt, *J. Chem. Phys.*, **25**, 467 (1956).

significant values of λ and of a component of $\vec{\mu}_e^\pi$ along the direction of $\vec{\mu}_m$. For example, if the C═C bond were made parallel to the C═O bond so that its atomic 2p orbitals pointed exclusively in the *y*-direction, the pertinent component of $\vec{\mu}_e$ could be increased by roughly a factor of 1.2; however, λ would decrease by about a factor of 4 because of the decrease in overlap. We also note that C_4 generally lies on or near the nodal plane of the non-bonding orbital. Therefore, there is no tendency for cancellation of overlap between the non-bonding orbital and the various parts of the π-system, as would be the case if the C═C bond were to straddle the C═O bond. Experimental support for the negligible importance of the atomic orbital at C_4 for the value of the mixing coefficient λ can be found in a comparison of the spectra of V and 7-isopropylidine-bicyclo[2.2.1]-heptane-2-one,[45] one enantiomer of which is shown in XVIII. Both compounds have virtually identical spatial dispositions of $OC_1C_2C_3$ (Fig. 3) but differ widely in the relative position of C_4. However, in the case of XVIII, the overlap of the non-bonding orbital with the atomic orbital at C_4 is also comparatively unimportant on grounds of distance, and both compounds exhibit virtually identical quadruplets (Table I).



XVIII



XIX

The preceding discussion applies immediately to norbornenone (V) and the santonides (II, III). For β,γ-unsaturated compounds containing π-chromophores other than ethylene, analogous descriptions hold, although the case of each such chromophore must be examined separately. In this connection, it is helpful to note that since the 300 mμ transition involves the highest bonding and lowest antibonding orbitals, the signs of the coefficients of the carbonyl 2p atomic orbitals and the 2p atomic orbital of the conjugated system most strongly involved in the coupling to the C═O group will be arranged as

$$\begin{array}{l} - \quad - \quad + \\ \overline{\qquad\qquad\qquad} \text{ zero of energy} \\ - \quad + \quad + \\ \text{C}\cdots\text{C=O} \end{array}$$

This particular array of signs will ensure the maximum number of nodes for a bonding level in the highest bonding orbital and the minimum number of nodes for an antibonding level in the lowest antibonding orbital upon formation of the composite chromophore.

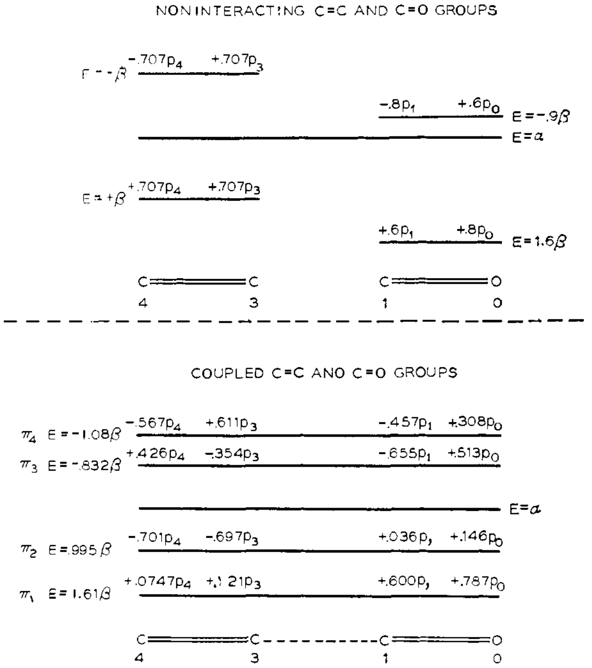


Fig. 17.—Energy levels and wave functions assumed for non-interacting and weakly interacting C═C and C═O groupings in bicycloöctenone.

The situation for dimethyldibenzsuberone (I) is similar to that for bicycloöctenone (IV). When the phenyl rings occupy the far negative octants, the p-orbitals on the carbons in the β-positions bear a relationship to p_0 and p_1 of the C═O group comparable to that of p_3 in bicycloöctenone. Also, simple semiempirical calculations indicate a bonding orbital of the proper energy that can mix with the non-bonding orbital of the carbonyl as described previously for bicycloöctenone, and hence leads to a positive value for λ. Again, the coefficient of the highest bonding and lowest anti-bonding orbitals demand that $\vec{\mu}_e$ have a positive *z*-component (it actually lies along the positive *z*-axis in this case) and hence that *R* be negative. In the case of the open-chain α-phenyl ketones, the contribution to $\vec{\mu}_e^\pi$ of the benzene ring will tend to lie along the bond connecting the α-carbon with the ring. Again, for conformers approximating Fig. 3, this means a significant component of $\vec{\mu}_e^\pi$ along the direction of $\vec{\mu}_m$.

The compound 7-isopropylidine-dehydronorcamphor (XIX) which also shows an enhanced absorption,[46] is interesting in that a given enantiomer has a C═C unit in both a left- and a right-hand octant. However, calculations of the type described above indicate that the π→π*-transition responsible for the enhanced absorption would involve principally the endocyclic double bond. Hence for the enantiomer shown (XIX) we would predict a positive long-wave length Cotton effect.

(45) Prepared by semi-hydrogenation of XIX (P. R. Story, unpublished results). The structure is confirmed by infrared and n.m.r. spectra. We are grateful to Dr. Story for placing this information at our disposal.

(46) C. H. DePuy and P. R. Story, *J. Am. Chem. Soc.*, **82**, 627 (1960), report $\lambda_{\max}^{\text{EtOH}}$ 308 mμ (ε 423); see Table I.