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EMPIRICAL CALCULATIONS
PERTAINING TO THE OPTICALLY ACTIVE AROMATIC CHROMOPHORE IN RIGID SYSTEMS

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Abstract—An empirical approach to the calculation of ORD and CD curves of the Amaryllis alkaloids crinine and crinane is presented. Utilization of UV and ORD data allows calculation of CD maxima which afford insight into the degree of overlap of ORD "tails". The calculated $A_{1g} \rightarrow B_{2u}$ transition of these compounds allows the contribution of the allylic moiety to be evaluated. The amplitude and sign of the Cotton effects due to functional groups affording transitions which cannot be directly observed can be estimated from these calculations. These can be correlated with stereochemistry.

In an excellent recent survey on ORD and CD of aromatic compounds[2] it was noted that very few theoretical aspects of rotatory phenomenon have been investigated. This is especially true when considering aspects of optical rotation which concern organic chemists. Moscowitz[3] has carried out elegant calculations on steroid molecules utilizing computer techniques and Klyne[4] has used a much simpler approach in evaluating chromophore contributions in keto steroids. Schellman[5] has recently published a fundamental paper on symmetry rules in aromatic compounds, while Kotra[6] *et al.*, and DeAngelis[7] and Wildman[8] have published quadrant rules for predicting the absolute configuration of aromatic compounds.

However, there have been no published examples of simple "back of the envelope" type calculations which allow one to construct an ORD or CD curve, from which valuable stereochemical information can be gleaned. We would like to demonstrate that in compounds containing single rigid aryl chromophores perturbed by dissymetric surroundings, one can carry out calculations which allow assessment of the contribution of a high energy transition to the total ORD spectrum. We shall demonstrate that either the equations of Kuhn[9] or Moscowitz[10] can be profitably utilized in the above manner.

The Amaryllis alkaloids crinine[11] and crinane[12] were chosen as models for these calculations. However, any given rigid system in which the aromatic transitions are well characterized can be treated similarly.

A series of ORD and CD curves can be constructed allowing the assignment of relative stereochemistries to functional groups which absorb in high energy regions of the spectrum and thus appearing as "tails" in the observed ORD curves.

Figs. 1 and 2 show the ORD, CD and UV* spectra of crinine. The 296 mμ aromatic absorption maximum in the UV spectrum gives rise to a dispersion which reaches a

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* Most of the Amaryllis alkaloids containing the methylenedioxy chromophore give rise to UV spectra very similar to that of crinine, and therefore the UV spectrum in the Fig. 2 may be taken as representative of this group of alkaloids.

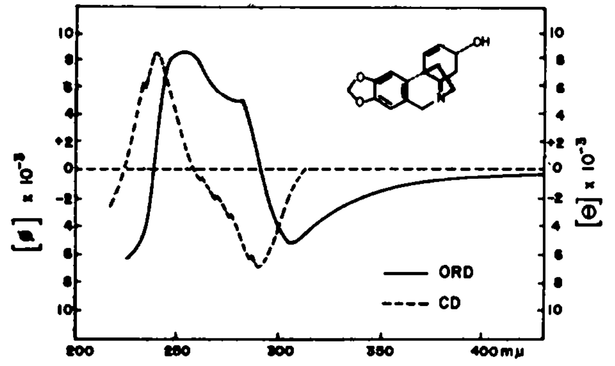

Fig. 1 ORD and CD of orinine.

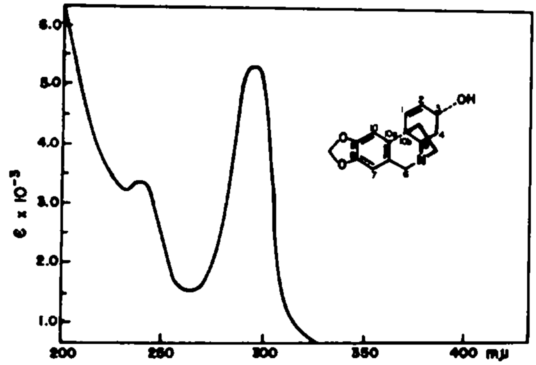

Fig. 2 UV spectrum of crinine.

negative maximum at 305 mμ in the ORD spectrum of crinine. The crossover points at 296 mμ and 240 mμ correspond to the UV absorptions seen at these same wavelengths. The CD spectrum corroborates the above assignment since both crossover points approximate the centers of the dichroism maxima.[13] By far the most valuable information concerning the optically active *benzene* ring is obtained from the CD measurements, since the aromatic ellipticities are usually of opposite sign and are well separated. In some cases the use of ORD data only can lead to ambiguous conclusions.* The CD maxima occur at the same wavelength as the UV maxima and spectra of the aromatic Cotton effects are obtained which are free of the uncertainties introduced by "tailing" in rotatory dispersion studies.

The amplitude of benzene chromophore in the ORD spectra increases rapidly in going from dihydrocrinine (Fig. 3) to crinine. This is likely due to homoconjugation of the C_1—C_2 double bond and the benzene ring.[14] Crinane (Fig. 4) represents the parent compound in the 5, 10b-ethanophenanthridine series and contains neither the OH group nor the double bond. It shows normal dichroism and dispersion curves with a

[*] With only rotatory dispersion measurements available the sign of the true aromatic bands cannot be conclusively determined. When a sign change of the $A_{1g} \rightarrow B_{2u}$ band occurs, as in powellane, it is not possible to unambiguously assign this to a change in sign of the aromatic Cotton effect or to a change in sign of some other chromophore. This is discussed in detail in Ref. 7.

similar decrease in the amplitudes relative to crinine. However, OH loss cannot account for the total decrease in the CD maxima, as it is well known that the dichroism of the aromatic ring at 295 mμ is not effected by a chromophore in the 210 mμ region.*[15] (−) Crinine, and (−) crinane may serve as model systems for the methylenedioxy group of 5,10b-ethanophenanthridine alkaloids. We chose these compounds to study the nature of their ORD spectra.

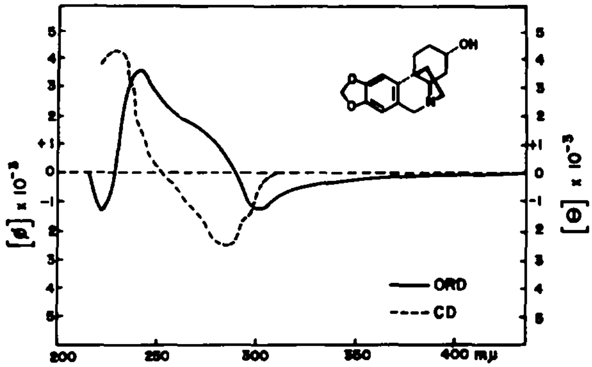

Fig. 3 ORD and CD of dihydrocrinine.

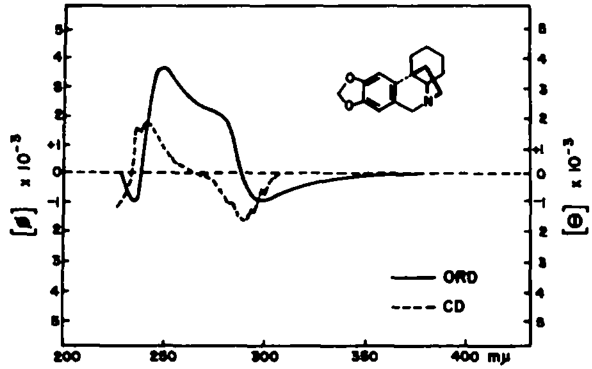

Fig. 4 ORD and CD of crinane.

In crinine there are asymmetric centers at positions 3, 5 and 10b. Absorptions at positions 5 and 10b are not observed in the usual type of UV spectrophotometer, while the allylic OH absorption can be seen only with difficulty. We have observed that the benzene chromophore gives rise to two ORD dispersions and CD ellipticities in a readily accessible portion of the spectrum. The two optically active benzene bands and the band due to the alcohol function provide the dispersions necessary to construct ORD curves for these compounds. From chemical evidence[17] it is

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* Since homoconjugation in these compounds effects the amplitude[16] of the Cotton effects and not the sign or λ_{max} position, it may be assumed to remain constant throughout any given structural class of compounds and its contribution can be minimized. This is discussed in more detail below.

known that the benzene ring and the alcohol group are *cis* to each other. Assuming that the first (296 mμ) benzene dispersion in (−) crinane and the OH group dispersion of crinine are of the same sign, the ORD curve of crinine may be constructed by simply superimposing the large OH dispersion upon those due to the benzene bands. This procedure has been carried out for crinane and crinine and is shown in *a* and *b* below. The composite curves agree well with the experimental ones. (Fig. 5). If the OH dispersion were assumed to be positive, the ORD curve of crinine would afford a maximum at 303 mμ *less than* that of crinane. The overall shape of the ORD spectrum of crinine would also be quite different. However, it has been shown[7] that while the OH function of crinine has a negative dispersion, epicrinine (epimeric at C_3) affords a *more* negative Cotton effect thus grossly changing the shape of the ORD spectrum.* The assignment of a negative sign to the α-OH in crinane is in accord with similar ones made in the steroid field. These assignments were made both for secondary and allylic alcohols.[18, 19]

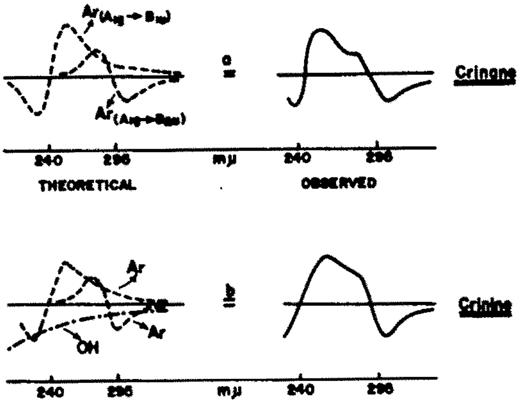

FIG. 5

Examination of the ORD curve of crinane reveals two pertinent facts. (1) The shape of the curve is quite similar to that of crinine between 375 and 225 mμ, which would tend to corroborate the statement that the Cotton effects arising from the two optically active benzene bands are the primary contributors to the dispersion curves in this region.[2] The peak at 250 mμ is much more pronounced in crinane than in crinine, which suggests that in crinane the main shape of the curve is derived from the two S-shaped dispersions of benzene as indicated previously. The decrease in amplitude of crinane relative to crinine is most likely due to removal of the double bond, OH group and homoconjugation. This same decrease is apparent in analogous compounds of the morphine series.[15] The dichroism curve of crinane has been discussed above.

Kuhn[9] and Moscowitz[10] have developed equations which permit the calculation of a number of properties of optically active molecules. Eq. 1 is that of Kuhn which he utilized for calculations of the properties azidopropionicdimethylamide [$CH_3CHN_3CON(CH_3)_2$].

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* A detailed discussion of the ORD spectra of the Amaryllis alkaloids shall be the subject of a forthcoming publication.

$$\Phi^0_{\text{cont.}} = 3723\, g_0 E_{\max} \frac{f}{f_0} \left\{ \exp\left[- \left(\frac{f_0 - f}{\Theta} \right)^2 \right] \int_0^{f_0 - f/\theta} e^{x^2}\, dx - \frac{\theta}{2(f_0 - f)} \right\} \tag{1}$$

where:

$\Phi^0_{\text{cont.}}$ = molecular rotatory power in region of absorption band;

g_0 = anisotropy factor at f_0;
f_0 = frequency at the center of the absorption band;
$E_{\max}$ = value of the molecular absorption coefficient corresponding to the center of the absorption band;
E = absorption coefficient of racemic substance for ordinary light;
f = frequency at which rotatory contribution (ORD) is a maximum;
$[\Phi]^0$ = value of $\Phi^0_{\text{cont.}}$ for $f = f_0$ (in circular degrees);
Θ = parameter related to the half width of an absorption band by $f'' = 1{\cdot}665$;
f'' = half width of an absorption band;
$E_1 - E_r = \Delta E$ = circular dichroism.

Kuhn defines the anisotropy factor, g_0, as shown in Eqs (2) and (3).

$$g_0 \cong \frac{[\Phi]^0}{2014\,(E_{\max})} \tag{2}$$

$$g_0 = \frac{E_1 - E_r}{E} = \frac{\Delta E}{E} \tag{3}$$

$$E = E_{\max} \exp\left[- \left(\frac{f_0 - f}{\Theta} \right)^2 \right] \tag{4}$$

The Amaryllis alkaloids crinine and crinane were subjected to Kuhn's treatment. Both of these compounds have a well defined absorption band at 296 mμ and both, as do all of the alkaloids with this ring system, have rigid structures. This fact eliminates any conformational and rotational changes which would otherwise have to be considered. Equation 2 was used to calculate g_0 for crinine and crinane. This was then substituted into equation 3 ($E = E_{\max}$ for the Amaryllis) and a CD maxima was calculated for each compound at f_0. In order to check the validity of such calculations eight other compounds were examined. The results are shown in Table 1.

The disagreement between the calculated and the observed values for (−) crinane suggests that the aromatic dispersions overlap by about the same amount as the calculated and observed CD maxima are in error, i.e. 25%. Since the two bands are opposite in sign (antipodal), and the CD curves were calculated from experimental ORD spectra with overlapping tails, it is apparent that the *observed* CD at 305 mμ for crinane *must* be larger than the calculated one. Overlapping bands are less a problem in the CD spectra and a much better reflection of the actual shape of the curve can be obtained. Consequently the data for crinine shows that the calculated value is 20% *larger* than observed. This is in accord with assigning a negative sign to the hydroxyl dispersion of this compound.

We can utilize crinine as an example to demonstrate that homoconjugation effects can be neglected. $[\Phi]$ is read from the ORD spectrum of any given compound, and

TABLE 1. CALCULATED CD MAXIMA FOR SELECTED ALKALOIDS

Compound	Calculated CD	Observed CD	% Difference
Crinine	−9250	−7300	+20
Crinane	−1120	−1500	+25
Powelline	−1800	−1620	+5
Powellane	+1230	+850	+30
Vittatine	+9300	+7900	+20
Crinamine	+14,700	+12,000	+22
6-Hydroxycrinamine	+10,700	+9600	+10
Haemanthidine	+7800	+9600	−20
Haemanthamine	+9600	+11,900	−20
Biophanidrine	−1430	−1200	+7

since this experimental value necessarily includes any contribution from homoconjugation the CD spectrum calculated utilizing [ϕ] shall also reflect homoconjugation. The observed experimental CD again necessarily reflects homoconjugation. Therefore even though both values, i.e. calculated and observed CD are not correct in the absolute sense, they both take into account to the same extent any homoconjugative effects reflected in the spectra, and the value designated as % difference reflects *other* effects discussed below.

The next calculations carried out derived the shape and amplitude of the 296 mμ aromatic absorption band when separated from the dispersions of other chromophores. Equation 1 was used for this and the results are given in Tables 2 and 3. The disagreement between calculated and observed values emphasizes the fact that the experimental spectra reflect contributions from all chromophores, while the calculated values attempt to isolate only 296 mμ aromatic dispersion. There is good agreement between observed and calculated values at the maxima only. This is to be expected since except for very low wavelength contributions the aromatic dispersions are the major contributors to the spectrum in the 250 to 350 mμ region of the spectra.

The constant 3723 which Kuhn utilized in his azidopropionic dimethylamid calculations is not the most suitable one for calculations in the Amaryllis series.

TABLE 2. CALCULATED ROTATORY DISPERSIONS FOR CRINANE AT 296 mμ UTILIZING KUHN'S METHOD

Wave length (mμ)	Calculated value of Φ^0	Observed value of Φ^0
350	−240	−140
340	−300	−165
330	−430	−220
320	−640	−440
310	−870	−890
300	−650	−900
290	+450	+130
280	+970	+1170 (Sh)
270	+720	+2170
260	+440	+2800
250	+310	+3600

TABLE 3. CALCULATED ROTATORY DISPERSIONS FOR CRININE AT 296...mμ UTILIZING KUHN'S METHOD

Wavelength (mμ)	Calculated value of Φ°	Observed value of Φ°
350	−1820	−650
340	−2360	−810
330	−3400	− 220
320	−4970	−1700
310	−6000	−3900
300	−2870	−5600
290	+3800	−3400
280	+6600	+8130 (Sh)
270	+4780	+8900
260	+300	+9300
250	+1950	+9000

In an effort to refine our calculations a new constant was derived. The data compiled in the calculations of CD maxima done previously were utilized for this purpose. The per cent difference found in the calculated versus the observed values of the CD maximum of crinane reflects the effect of the 240 mμ benzene band and other Cotton effects on the 296 mμ band. In compounds possessing chromophores other than aromatic the per cent difference reflects the effect on the 296 mμ band. In order to include these factors in any new constant which would be general for the 5,10b-ethanophenanthridine alkaloids the following equation was used; (Eq. (5)).

$$\phi_{\text{max}} = \phi_{\text{obs}} \pm \phi_{\text{obs}}(n) = K g_0 \, E_{\text{max}} \frac{f}{f_0} \left[e^{-q^2} \int_0^{f_0 - f/\theta} e^{x^2} \, dx - \frac{\Theta}{2(f_0 + f)} \right] \tag{5}$$

Φ_{max} is equal to the observed value of the dispersion in a given compound plus or minus this observed value times the per cent difference. This is shown in Eq. (6), where

$$\phi_{\text{max}} = \phi_{\text{obs}} \pm \phi_{\text{obs}}(n) \tag{6}$$

Since the calculation is for $[\phi]_{\text{m}\mu}$, all of the variables in equation 5 are known except the value of the integral and K, the new constant. The integral term can be set at its maximum value which is 0·54 for the compounds under scrutiny. An average value of the term $\Theta/2(f_0 + f)$ was found to be 0·01. Actually the final answers would be changed very little if this last term were neglected. The constant (K) calculated in the above way, should represent the value found for a completely isolated absorption band which reaches its maximum rotational value at some frequency f and where $M = 0$ at f_0. Experimentally $M \neq 0$ at f_0 and f is not at Kuhn's f_*. Both are displaced according to the degree of band overlap. This displacement is small in crinane, but becomes larger in more substituted compounds. Constants were calculated for four compounds and these plus an average value with its average deviation are shown in Table 4.

The error in these values is 11 %, which is the same order of magnitude as the usual experimental errors. Computerized calculations would undoubtedly provide more refined results.

TABLE 4. CALCULATED CONSTANT FOR DISPERSION EQUATION

Compound	Calculated constant (K)
Crinane	4850
Crinine	3950
Crinamine	3730
6-OH crinamine	4780
Average	4325 ± 490

Moscowitz[10] has used a slightly different approach in developing equations which can be used to calculate partial dispersions. The final equations which Moscowitz arrives at are shown in Eqs (7) and (8).

$$[\Phi]_k^0 = \frac{2[\theta_k^0]}{\sqrt{\pi}} \left\{ \exp\left[-\left(\frac{\lambda - \lambda_k^0}{\Delta^0 K}\right)^2\right] \frac{\lambda - \lambda_k^0}{\Delta K} e^{x^2}\,dx - \frac{\Delta^0 K}{2(\lambda - \lambda_k^0)} \right\} \tag{7}$$

$$[\theta]_k = \frac{Rk}{0{\cdot}696 \times 10} - 42 \frac{\lambda_{k2}^0}{\Delta_k^0} \left\{ \exp\left[-\left(\frac{\lambda - \lambda_k^0}{\Delta^0 K}\right)^2\right] \lambda - \lambda_k^0\, e^{x^2}\,dx - \frac{\Delta^0 K}{2(\lambda + \lambda_k^0)} \right\} \tag{8}$$

where:

$[\theta_k^0]$ = dichroism at λ_{max};
λ = wave length where calculation being made;
λ_k^0 = wave length at center of absorption band;
$\Delta^0 K$ = half width of absorption band at half height (obtained by measurement from UV spectrum);
$[\theta]_k^0$ = dispersion (molecular rotation) at wave length where calculation being made;
R_k = rotational strength = $0{\cdot}696 \times 10^{-42}(\sqrt{\pi})\,\theta_k\,(\Delta_k^0/\lambda_k^0)$.

Either one of these can be used to calculate the partial dispersion of the 296 mμ benzene band. Eq. (8) was chosen in the present work as it involved the calculation R_k, the rotational strength. It was of interest to compare the rotational strengths calculated for these aromatic chromophores with those calculated for a number of ketone chromophores. Since the values of the rotational strengths are very small, reduced rotational strength $[R]$ are tabulated in Table 5. The reduced rotational strength is related to the rotational strength as shown in Eq. 9.

$$[R] = (100/u_0 u_d)\,R_k \cong 1{\cdot}08 \times 10^{40}\,R_k \tag{9}$$

TABLE 5. CALCULATED REDUCED ROTATIONAL STRENGTHS

[R] (aromatic)		[R] (carboxyl)[10]	
Crinine	−11·2	2,2,5 trimethylcyclohexanone	+6·7
Crinane	−1·18	2,2 dimethylcyclohexanone	+1·8
Powelline	−2·07	trans-9-methyl-3-decalone	−3·6
Powellane	+1·25	cis-9-methyl-6-decalone	+0·73

where

u_0 = magnetic dipole moment in Bohr magnetrons;
u_d = electric dipole moment in Debyes.

In general it seems that the rotational strengths of the aromatic and carbonyl chromophores are comparable. When applied to the 296 mμ benzene band, Eq. (8) gives results which are in good agreement with those obtained using the constant derived for the Amaryllis and used in Kuhn's equation. A comparison of these results is made in Tables 6 and 7, and the curves from the calculated constant are shown in Fig. 6. It should be noted from the tables that the maximum rotational values for crinane come at the same wave lengths for both the calculated and observed cases. This is not the case in the crinine calculations. This discrepancy is due probably

TABLE 6. CALCULATED DISPERSIONS OF CRINANE AT 296 mμ UTILIZING MOSCOWITZ'S METHOD AND THE CALCULATED CONSTANT (K)

Wave length (mμ)	Calc. const. (4325)	Moscowitz	Observed
350	$\Phi^\circ = -280$	$\Phi^\circ = -310$	$\Phi^\circ = -140$
340	−340	−380	−165
330	−500	−520	−220
320	−740	−770	−440
310	−1020	−1040	−890
305	−900 (Fig. 6)	−900 (Fig. 6)	−1080
300	−650	−635	−900
290	+525	+500	+130
280	+1120	+1020	+1770 (Sh)
270	+835	+730	+2170
260	+510	+430	+2800
250	+350	+390	+3600

TABLE 7. CALCULATED DISPERSIONS OF CRININE AT 296 mμ UTILIZING MOSCOWITZ'S METHOD AND THE CALCULATED CONSTANT (*K*)

Wave length (mμ)	Calc. const. (4325)	Moscowitz	Observed
350	$\Phi^\circ = -2140$	$\Phi^\circ = -1810$	$\Phi^\circ = -650$
340	−2800	−2300	−810
330	−4050	−3380	−1220
320	−5900	−5400	−1700
310	−7100	−7400	−3900
305	7200 (Fig. 6)	7200 (Fig. 6)	−6600
300	3400	−3060	−5600
290	+4470	+4470	−3400
280	+7850	+7000	+8130 (Sh)
270	+5650	+4800	+8900
260	+3500	+3000	+9300
250	+2300	+2100	+9000

to a shift in the crossover point of the experimental ORD curve caused by the additional OH dispersion. The implications of these calculations are as follows:*

At the maximum rotational values of the 296 mμ benzene band in crinine and crinane the agreement between calculated and observed spectra is very good. This may imply that at this point the slope of any background tail is small relative to the aromatic Cotton effect. This combined with the fact that the rotational values of the tails are small at these wavelengths (300 → 350 mμ) may account for the observed agreement at 305 mμ. At longer wavelengths from the maxima it can be seen that the calculated Cotton effects are always larger than the observed. This is in agreement with the calculated CD spectra presented earlier and with assigning a negative Cotton effect to the α allylic hydroxyl moiety. From the close agreement of the observed and calculated maxima in crinane, it must be concluded that there is either very little overlap of the $A_{1g} \to B_{1u}$ and $A_{1g} \to B_{2u}$ electronic transition or that whatever overlap there is is negated by a negative Cotton effect of approximately the same size.

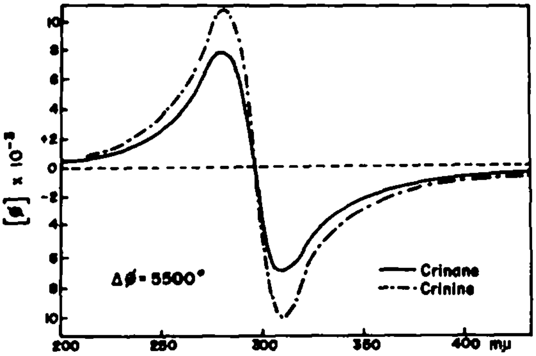

Fig. 6 Calculated dispersions of crinine and crinane.

The calculations presented here attempt to separate one Cotton effect from another in order to gain insight into where one electronic transition ends and a second begins. If this can be done, it should then be possible to calculate the Cotton effects of chromophores which cannot be measured directly. Eq. (10) presents a method of accomplishing this for crinane.

$$ {}^{\lambda}_{\text{obs}} = {}^{A_{1g}\to B_{2u}}_{\lambda} + {}^{A_{kg}\to B_{1u}}_{\lambda} + \phi_B \qquad (10)$$

where:

$\phi^{\lambda}_{\text{obs}}$ = observed ORD spectrum;
$\phi^{A_{1g}\to B_{2u}}_{\lambda}$ = calc. dispersion of $A_{1g} \to B_{2u}$ benzene band;
$\phi^{A_{1g}\to B_{1u}}_{\lambda}$ = calc. dispersion of $A_{1g} \to B_{1u}$ benzene band;
ϕ_B = background contributions.

Once the values of $\phi^{A_{1g}\to B_{1u}}_{\lambda}$ and $\phi^{A_{1g}\to B_{2u}}_{\lambda}$ are known it becomes possible to add terms to the right-hand side of the equation as new optically active moieties are added to

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* Since all of the calculations resulted in approximately the same results we shall not distinguish between them in any further discussion. However, the numerical examples used for illustration are those calculated from $K = 4325$.

the molecule. It should be a relatively simple matter then to assign values to α and β substituents in known systems and utilize these to determine the stereochemistries in unknown ones.

The complete dispersion of the $A_{1g} \rightarrow B_{2u}$ transition has been calculated in crinine The contribution of the $A_{1g} \rightarrow B_{1u}$ dispersion can be obtained in a number of ways. It can be calculated in exactly the same manner as the $A_{1g} \rightarrow B_{2u}$ transition, or it can be obtained in a very approximate manner by simply sketching it in on a recorded spectrum where the $A_{1g} \rightarrow B_{2u}$ band has already been superimposed. This method would neglect any contribution from background dispersions. Thirdly one can use the calculated values of the $A_{1g} \rightarrow B_{2u}$ band and utilizing Eq. (10) calculate the term $\phi^{A_{1g} \rightarrow B_{1u}} + \phi_B$. This is shown in Fig. 7 for a few points. (250 → 280 mμ). Although only an approximation Fig. 7 allows one to decide that there are maxima at ca. 280 mμ and ca. 250 mμ.

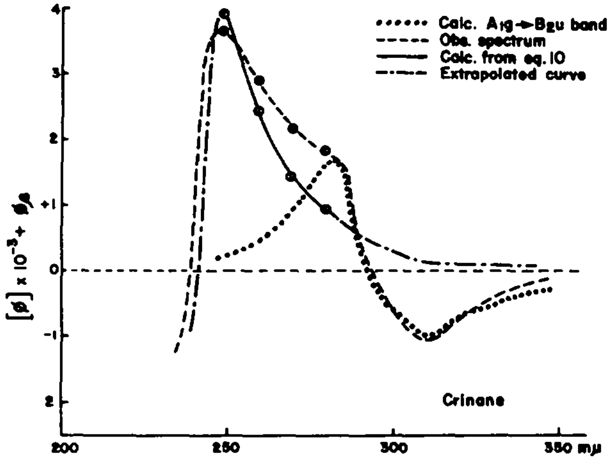

FIG. 7 Calculated dispersions superimposed on the observed spectrum of crinane.

If a term for the allylic alcohol moiety is added (Eq. (11)) one can now calculate its contribution to the total spectrum of crinine. In the background term are included the asymmetric centers at C_5 and the 205 mμ

$$\phi^{\lambda}_{\text{obs}} = \phi_{\lambda}^{A_{1g} \rightarrow B_{2u}} + \phi_{\lambda}^{A_{1g} \rightarrow B_{1u}} + \phi_{AA} + \phi B \tag{11}$$

benzene transition. This term will cancel between any two equations. This is shown in Eq. (12) which is used to calculate the contribution of the HC = C—CH—OH moiety. This calculation is carried out at 305 mμ since this is the maximum of the crinine dispersion and subject to the least error. As can be seen from Fig. 6 a difference of only 2–3 mμ (300 → 297 mμ) results in a change in rotation of 3500° whereas at the maxima a change from 304 → 307 mμ results in a very small change.

$$\begin{gathered}
[\phi_{305}^{\text{crinine}} - \phi_{305}^{\text{crinane}}] = [\phi_{A_{1g} \rightarrow B_{1u}}^{\text{crinine}} - \phi_{A_{1g} \rightarrow B_{1u}}^{\text{crinane}}] + [\phi_{A_{1g} \rightarrow B_{2u}}^{\text{crinine}} - \phi_{A_{1g} \rightarrow B_{2u}}^{\text{crinane}}] + \phi_{AA} \\
[-6600^\circ + 1080^\circ] = [-7200 + 900^\circ] + [9000^\circ - 3600^\circ] + \phi_{AA} \\
\phi_{AA} = -4620^\circ
\end{gathered} \tag{12}$$

Use of Eq. (12) demonstrates that some 900° are due to dispersions other than the aromatic ones. The validity of the value −4620° is corroborated by the experimental fact that dihydrocrinine affords an ORD spectrum with $\Phi_{305} = -1360°$. This represents a loss of 4100° which can be attributed to removal of the double bond and an apparently great deal of homoconjugation. Reduction of dihydrocrinine to crinane further reduces the rotation by 450 degrees. Chemical reduction results in the sequence:

$$\begin{array}{ccccc} \text{Crinine} & \longrightarrow & \text{H}_2\text{-Crinine} & \longrightarrow & \text{Crinane} \\ \phi_{305} = -6600° & & \phi_{305} = -1400° & & \phi_{305} = -1100° \end{array}$$

whereas the hypothetical reduction carried out *via* equation 12 resulted in

$$\begin{array}{ccc} \text{Crinine} & \longrightarrow & \text{Crinane} \\ \phi_{305} = -6600° & & \phi_{305} = -2000° \end{array}$$

Considering the approximations utilized in the method, these results are encouraging.

The sample calculations described above are noteworthy in that they need be done only once for a given family of compounds. If one calculates the contribution from the bare nucleus and those from one or two more highly substituted derivatives, it then becomes possible to assign the configuration of functional groups utilizing this data and superimposing the dispersion of the particular moiety one is concerned with. A representative number of examples of this procedure can be found elsewhere.[7]

We would once again like to stress that these calculations represent not so much new calculations as a practical utilization of well known equations, which can afford useful information with a minimum amount of effort.

EXPERIMENTAL

All of the ORD spectra have been recorded on a Jasco Model 5 ORD spectrophotometer and the CD spectra on a modified[20] Jouan dichrograph. The solvent used in all cases was methanol unless stated otherwise. The units of rotation used are degrees per decimeter; those of ellipticity are degree $-\text{cm}^2$ per decimole. In both cases these are simply recorded as degrees.

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