energy (electron ejected from argon by He(I)), there is no sign of any of the clear vibrational structure observed on the first and fourth bands in our spectrum, where a resolution of only 20 meV is employed.

The second point to note is that on the basis of two sharp steps observed in their spectrum (quoted as 12.728 ± 0.001 eV and 12.803 ± 0.005 eV) the authors reverse the assignment of the 3_{ag} and $1b_{2u}$ orbitals (3_{ag} and $1b_{3u}$ in their notation). These two sharp peaks are not observed in our spectrum, the second vertical IP being 13.3 eV (see Table I), and it is believed[19] that they are due to an HCl impurity (first IP 12.74 ± 0.01 eV and 12.82 ± 0.01 eV; a spin-orbit doublet[20]). Besides removing any reason for reversing the orbital assignment this also implies that their error limits must be $\geq \pm 0.002$ eV on the first HCl peak, not ± 0.001 eV, and ≥ 0.007 eV on the second peak, not ± 0.005 eV.

[19] D. W. Turner, private communication.

[20] H. J. Lempka, T. R. Passmore, and W. C. Price, *Proc. Roy. Soc., Ser. A*, **304**, 53 (1968).

Circular Dichroism of Nucleoside Derivatives. VIII. Coupled Oscillator Calculations of Molecules with Fixed Structure

Warren H. Inskeep, Daniel W. Miles, and Henry Eyring

Contribution from the Department of Chemistry
and Institute for the Study of Rate Processes, University of Utah,
Salt Lake City, Utah 84112. *Received October 10, 1969*

Abstract: A method of calculating rotational strengths by a bond–bond coupled oscillatory theory is described. The technique is applied to a variety of specially chosen molecules to check the theory at various levels of approximation. Good agreement with experiment, particularly in the case of the cyclonucleosides, suggests that coupled oscillator theory accounts for most of the observed optical activity in the pyrimidine nucleosides. The calculation is particularly useful for structure determination because of its simplicity and complete dependency on bond orientations within a molecule.

In a recent survey[1] on ORD and CD of aromatic compounds it was noted that very few of the theoretical aspects of Cotton effects attributed to electronic transitions in symmetric aromatic chromophores bonded to an array of chemical groups with transitions in the far-uv region have been investigated. While it is generally accepted that the Rosenfeld equation[2] gives the correct quantum mechanical result for the optical rotatory dispersion of any optically active molecule and the theories of Condon, Altar, and Eyring[3] and of Kirkwood[4] provide expressions governing the relationship between optical rotatory strengths and chemical structure, the extension of these theories to more complex chromophores remains to be conceived. Some progress along these lines has been made recently by several investigators employing the one-electron theory of optical rotation. Caldwell and Eyring[5] have calculated the sodium D-line optical rotation of 1-methylindan. More recently, Moscowitz[6] has employed qualitative one-electron concepts to explain the enhancement of the ^1L_b Cotton effect when the benzene ring is substituted with oxygen or nitrogen. Kuriyama, *et al.*,[7] and DeAngelis[8] have published quadrant rules for predicting the absolute configuration of aromatic compounds based on symmetry rules that arise in the one-electron theory.

Nevertheless, there is some evidence that the coupled oscillator mechanism can make significant contributions to these Cotton effects. Höhn and Weigang have demonstrated that "dynamic coupling" terms can be dominant in appropriate ketone molecules.[9] In previous papers of this series,[10] the $\pi-\pi^*$ nature of the absorption spectra of the ribonucleosides (and some 300 closely related derivatives) has been established in the 190–300-nm range. To assign absolute configurations to these molecules, resort has been made to the Kirkwood–Tinco[11] polarizability expression for the rotational strength. This treatment utilizes bond polarizabilities to bring in the effects of the vicinal group upon the planar chromophore. The chromophore electronic transition moment was either calculated from simple LCAO MO theory or obtained from experimental data. This moment was then coupled to each bond of the vicinal group *via* a dipole–dipole interaction potential. The magnitudes of the calculated rotational strengths were sufficiently large to encourage further pursuit of a coupled oscillator interpretation of the CD data.

In the present communication we give an improved scheme to obtain coupled oscillator rotational strengths of nucleosides, as well as all other molecules containing

[1] P. Crabbe and W. Klyne, *Tetrahedron*, **23**, 3449 (1967).

[2] L. Rosenfeld, *Z. Phys.*, **52**, 161 (1928).

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

[4] J. G. Kirkwood, *ibid.*, **5**, 479 (1937).

[5] D. J. Caldwell and H. Eyring, *Ann. Rev. Phys. Chem.*, **15**, 281 (1964).

[6] A. Moscowitz, A. Rosenberg, and A. E. Hansen, *J. Amer. Chem.*, **87**, 18183 (1965).

[7] K. Kuriyama, T. Iwata, M. Moriyama, K. Kotera, Y. Hanada, R. Mitsui, and K. Takeda, *J. Chem. Soc., B*, 46 (1967).

[8] G. G. DeAngelis, Ph.D. Thesis, Iowa State University, Ames, Iowa, 1966.

[9] E. G. Höhn and O. E. Weigang, Jr., *J. Chem. Phys.*, **48**, 1127 (1968).

[10] D. W. Miles, M. J. Robins, R. K. Robins, S. F. Hahn, and H. Eyring, *J. Phys. Chem.*, **72**, 1483 (1968); D. W. Miles, R. K. Robins, and H. Eyring, *ibid,*, **71**, 3931 (1967).

[11] I. Tinoco, *Advan. Chem. Phys.*, **4**, 113 (1962).

a locally symmetric chromophore attached asymmetrically to a saturated vicinal group. The approach is somewhat similar to the calculations of Moscowitz[12] and of Kemp and Mason[13] on inherently dissymmetric chromophores in that the transition moment of the chromophore is resolved along bonds (using the gradient operator) and then a bond-bond coupling is employed to get the rotational strength. This procedure has a twofold advantage over the earlier method. First, the geometry of the chromophore enters the calculation to a greater degree, and second, the gradient expression of the transition moment is consistent with the Kramers–Heisenberg[14] dispersion formula of quantum electrodynamics. The wave functions of the chromophore are obtained for the most part from the Pariser–Parr–Pople calculation of Adams and Miller.[15] The vicinal group is described empirically using experimental oscillator strengths and energies observed in the far uv as guidelines.

The technique of calculation is thoroughly outlined in the next section. In section II we apply the calculation to a variety of molecules, first considering an example that would *a priori* tax the approximations involved considerably less than the nucleosides. Then an example of an intermediate nature is discussed, and finally the technique is applied to four cyclouridines.

I. Theory

The nucleosides (and similar molecules) are conveniently divided into two parts, the unsaturated chromophore and the saturated vicinal group. When such a separation is used and a dipole–dipole interaction potential is assumed, the Kirkwood coupled oscillator theory[4] gives the rotational strength as

$$R_{\mathrm{a}} = \sum_{\mathrm{b}\neq\mathrm{a}} \frac{2\pi}{hc} \frac{\nu_{\mathrm{a}}\nu_{\mathrm{b}}\mu_{\mathrm{a}}{}^2\mu_{\mathrm{b}}{}^2}{(\nu_{\mathrm{b}}{}^2 - \nu_{\mathrm{a}}{}^2)} GF \tag{1}$$

where

$$GF = \left[\hat{e}_{\mathrm{a}}\cdot\hat{e}_{\mathrm{b}} - 3\frac{(\hat{e}_{\mathrm{a}}\cdot\vec{R}_{\mathrm{ab}}(\hat{e}_{\mathrm{b}}\cdot\vec{R}_{\mathrm{ab}})}{R_{\mathrm{ab}}{}^2}\right]\frac{\hat{e}_{\mathrm{a}} \times \hat{e}_{\mathrm{b}}\cdot\vec{R}_{\mathrm{ab}}}{R_{\mathrm{ab}}{}^3} \tag{2}$$

(No summation over vicinal groups is needed since we have only one.) The letter a designates not only the transition 0 → a (transition from the ground state, 0, to the excited state, a), but also indicates the chromophore group, and likewise b designates the vicinal group and its set of transitions from the ground state, 0 → b; $\hat{e}_{\mathrm{a}}$ is the unit vector in the direction of the electronic transition moment of the chromophore transition 0 → a, μ_{a} and ν_{a} are the corresponding magnitude and frequency; $\hat{e}_{\mathrm{b}}$, μ_{b}, and ν_{b} are the analogous quantities for all the transitions in the vicinal group; $\vec{R}_{\mathrm{ab}}$ is the distance between the two groups, directed from the chromophore, a, to the vicinal group, b.

The expression 1 as originally intended meant that the overall transition moment of the chromophore transition, 0 → a, was to be coupled to all of the overall transition moments in the vicinal group which are not degenerate with the 0 → a transition. However, in the approximation of taking only the lowest energy transition in the vicinal group, the summation indicated in eq 1 is not needed. Furthermore, the associative properties of vector multiplication allow the transition moment vectors to be broken down into any desirable set of components, and these components may be coupled by eq 1 and then summed to get the rotational strength. The transition moment in the chromophore is easily resolved into components along bonds, and an empirical procedure accomplishes the same thing in the vicinal group. Thus, one obtains a bond-bond coupling procedure to arrive at a coupled oscillator rotational strength calculation.

Chromophore Bond Transition Moments. The gradient expression for the *total* transition moment is

$$\vec{\mu}_{\mathrm{a}} = \frac{\sqrt{2}\beta_{\mathrm{m}}}{\pi\bar{\nu}_{\mathrm{a}}}\langle 0|\vec{\nabla}|\mathrm{a}\rangle \tag{3}$$

where β_{m} is the Bohr magneton (0.9273×10^{-20} cm esu), and $\bar{\nu}_{\mathrm{a}} = \nu_{\mathrm{a}}/c$. Expanding into a linear combination of atomic orbitals

$$\psi_0 = \sum_n c_n\phi_n \qquad \psi_{\mathrm{a}} = \sum_n c_n{}^*\phi_{\mathrm{n}}$$

there results

$$\begin{aligned}\vec{\mu}_{\mathrm{a}} &= \frac{\sqrt{2}\beta_{\mathrm{m}}}{\pi\bar{\nu}_{\mathrm{a}}}\sum_{\mathrm{r,s\ adjacent}}(c_{\mathrm{r}}{}^*c_{\mathrm{s}} - c_{\mathrm{r}}{}^*c_{\mathrm{s}})\vec{\nabla}_{\mathrm{rs}} \\ &\equiv \frac{\sqrt{2}\beta_{\mathrm{m}}}{\pi\bar{\nu}_{\mathrm{a}}}\sum_{\mathrm{r,s\ adjacent}}P_{\mathrm{rs}}\vec{\nabla}_{\mathrm{rs}}\end{aligned} \tag{4}$$

with $P_{\mathrm{rs}} \equiv (c_{\mathrm{r}}c_{\mathrm{s}}{}^* - c_{\mathrm{r}}{}^*c_{\mathrm{s}})$ called the transitional bond order.[13] Nonnearest neighbor contributions are small and assumed zero in deriving (4). Use also was made of the skew Hermitian properties of the integrals

$$\int_{\substack{\mathrm{all}\\ \mathrm{space}}}\phi_{\mathrm{r}}\vec{\nabla}\phi_{\mathrm{s}}\mathrm{d}\tau \equiv \vec{\nabla}_{\mathrm{rs}} = -\vec{\nabla}_{\mathrm{sr}} \tag{5}$$

which property is easily seen by an integration by parts. Ehrenson and Phillipson[16] have shown that these integrals over 2pπ Slater-type orbitals are given by

$$\langle 2\mathrm{p}\pi_{\mathrm{r}}\left|\frac{\partial}{\partial z_{\mathrm{s}}}\right|2\mathrm{p}\pi_{\mathrm{s}}\rangle = -\frac{\zeta_{\mathrm{s}}{}^7}{\zeta_{\mathrm{r}}{}^5}C_{01}{}^{101} \tag{6}$$

with ζ = (effective nuclear charge)/(principal quantum number). $C_{01}{}^{101}$ is one of the C functions of Ruedenberg, Roothaan, and Jaunzemis,[17] and has been given explicitly by them as

$$C_{01}{}^{101} = [\rho/5 + \rho^2/5 + \rho^3/15]e^{-\rho} \tag{7}$$

with

$$\rho = {}^1\!/_2(\zeta_{\mathrm{r}} + \zeta_{\mathrm{s}})R$$

and R is the internuclear distance. This is equivalent to the expression used by Moscowitz[12] in his work on hexahelicene, and is applicable only when both atoms have the same effective nuclear charge, $\zeta_{\mathrm{r}} = \zeta_{\mathrm{s}}$. When $\zeta_{\mathrm{r}} \neq \zeta_{\mathrm{s}}$, we must use the more lengthy expression

---

(12) A. Moscowitz, Ph.D. Thesis, Harvard University, 1957.

(13) C. M. Kemp and S. F. Mason, *Tetrahedron*, 22, 629 (1966).

(14) J. J. Sakurai, "Advanced Quantum Mechanics," Addison-Wesley, Reading, Mass., 1967.

(15) O. W. Adams and R. L. Miller, *J. Amer. Chem. Soc.*, **88**, 404 (1966); *Theor. Chim. Acta*, **12**, 151 (1968).

(16) S. Ehrenson and P. E. Phillipson, *J. Chem. Phys.*, **34**, 1224 (1961).

(17) K. Reudenberg, C. C. J. Roothaan, and W. Jaunzemis, Technical Report, Laboratory of Molecular Structure and Spectra, University of Chicago, 1952–1953.

$$C_{01}{}^{101} = 4\rho_s{}^{-4}(\kappa - 1)\{-(\kappa - 1)^2[36(\kappa + 1)^2 \times (1 + \rho_s) + 6(\kappa + 1)(2\kappa + 3)\rho_s{}^2 + 6(\kappa + 1)\rho_s{}^3 + \rho_s{}^4]e^{-\rho_s} + (\kappa + 1)^2 \times [36(\kappa - 1)^2(1 + \rho_r) + 6(\kappa - 1)(2\kappa - 3)\rho_r{}^2 - 6(\kappa - 1)\rho_r{}^3 + \rho_r{}^4]e^{-\rho_r}\} \quad (8)$$

where $\kappa = {}^1/_2(\tau + \tau)^{-1}$, $\tau = (\rho_r - \rho_s)/(\rho_r + \rho_s)$, $\rho_r = R\zeta_r$, $\rho_s = R\zeta_s$. (When these values are put into eq 6, the resulting integral is in units of reciprocal Bohr radii.) The values of interest of the $\vec{\nabla}_{rs}$ integrals are given in Table I over a range of appropriate internuclear distances. The effective nuclear charges were obtained from Slater's rules. Thus, if atoms r and s designate the atoms of bond i, then for the transition 0 → a the *component* of the transition moment along that bond is

Table I. $|\nabla_{rs}| \times 10^{-7}$ cm^{-1}

Internuclear distance, Å	$\nabla_{C,C}$	$\nabla_{C,N(1)}$[a]	$\nabla_{C,N(2)}$[a]	$\nabla_{C,O(1)}$[a]	$\nabla_{C,O(2)}$[a]
1.20	5.232	4.911	4.649	4.402	4.102
1.22	5.118	4.780	4.514	4.264	3.965
1.24	5.005	4.649	4.379	4.130	3.831
1.26	4.891	4.521	4.247	3.997	3.200
1.28	4.777	4.392	4.117	3.866	3.571
1.30	4.664	4.266	3.988	3.738	3.445
1.32	4.552	4.142	3.862		3.322
1.34	4.440	4.019	3.738		3.202
1.36	4.329	3.898	3.617		3.085
1.38	4.218	3.780	3.498		2.971
1.40	4.109	3.663	3.381		2.860
1.42	4.001	3.548	3.267		2.752
1.44	3.895	3.436	3.155		2.646
1.46	3.790	3.325	3.046		2.544
1.48	3.686	3.217	2.940		2.445
1.50	3.583	3.112	2.836		2.349

[a] N(1) indicates a nitrogen atom that contributes one 2pπ electron, etc.

$$\vec{\mu}_{ia} = \frac{\sqrt{2}\beta_m}{\pi\bar{\nu}_a} P_{rs}\vec{\nabla}_{rs} \quad (9)$$

directed from r to s.

Vicinal Group Bond Transition Moments. It is unfortunate that semiempirical calculations on σ-electron systems are not as reliable as those on π-electron systems, for then we could treat both the chromophore and vicinal group in the same manner and, hence, more nearly to the same level of approximation. There is, however, sufficient experimental evidence to get reasonable empirical values for the vicinal group transition properties.

Let us consider only the valence electrons in the vicinal system, and take the bonds as independent electron systems. As is well known, this division is generally permissible to first order in the estimation of bond lengths and heats of formation. That it is reasonable for other electronic properties has been demonstrated by the recent experimental and theoretical work of Raymonda and Simpson.[18] These authors noted that the lowest energy transition in saturated normal hydrocarbons demonstrated a Beer's law dependency of the extinction coefficient on the number of carbon-carbon bonds.

To each bond, j, we shall associate one effective transition moment, $\vec{\mu}_{jb}$, at a frequency ν_{jb}. That the direction of this transition moment can be taken along the bond is suggested by polarizability measurements. Though there is some disparity among the various magnitudes of the anisotropies, it is generally agreed that the polarizability along the bond is substantially greater than the polarizability perpendicular to the bond.[19-21] The estimate of the quantity $\vec{\mu}_{jb}$ is selected to reproduce the anisotropy of the polarizability of the bond under consideration. To do this we set the right-hand side of eq 1 equal to the Kirkwood polarizability expression, and obtain by cancellation

$$h\nu_0{}^2(\alpha_{33} - \alpha_{11}) = 2\nu_b\mu_{jb}{}^2$$

If we take $\nu_0 = \nu_b$ (ν_0 taken from our previous work), we can solve for μ_{jb}.

In our earlier work[10] we used LeFevre's[19] values for the polarizability anisotropies of the carbon-carbon bond and the carbon-hydrogen bond (α_{33} and α_{11}), but these values have been recently criticized because of the indirect methods used to obtain them.[21] Of the principle methods employed to determine bond anisotropies, only light depolarization measurements lead straightforwardly to molecular anisotropies and hence to bond polarizabilities. Denbigh's values,[20] which were determined in this manner, are consequently more widely accepted than those of LeFevre, and have been adopted here to calculate the effective bond transition moments (Table II). Denbigh did not determine the anisotropy of the carbon-oxygen bond, but he did show that the ratio of the transverse and longitudinal polarizabilities of C-X bonds, apart from the C-H bond, is practically constant at 0.56. He also provided an empirical equation which relates the longitudinal polarizability with the length of the bond, and the resulting anisotropy gives the values for the C-O bond shown in Table II.

Table II. Vicinal Bond Empirical Parameters

Bond	$\nu_{jb} \times 10^{-15}$, sec^{-1}	$\mu_{jb} \times 10^{18}$, cm esu
C-C	2.3	3.75
C-O	2.0	2.10
O-H	2.0	1.13[a]
C-H		0.0[b]

[a] In the examples we have used the values given for C-O for the O-H bonds in order to overestimate contributions from the latter bonds, since we wish to show these bonds are negligible calculations. [b] By assumption, as explained in text.

For C-H bonds, the anisotropies are small and less directional than for C-C bonds. Further, Raymonda and Simpson[18] have shown that the lowest energy transition due to this bond has a smaller oscillator strength than the C-C bond. Thus, C-H contributions would be relatively smaller than the others, and are assumed zero in the following calculations. (Even if this contribution were not zero, the near random orientations of the large number of C-H bonds would

---

(18) J. W. Raymonda and W. T. Simpson, *J. Chem. Phys.*, 47, 430 (1967).

(19) C. G. LeFevre and R. J. W. LeFevre, *J. Chem. Soc.*, 3549 (1961).

(20) K. F. Denbigh, *Trans. Faraday Soc.*, 36, 936 (1940).

(21) R. L. Jernigan and P. J. Flory, *J. Chem. Phys.*, 47, 1999 (1967).

Table III. Comparison of the Calculated and Experimental Spectra

No.	Molecule name	Transition		λ, nm	$f(r)$[a]	$f(\nabla)$[a]	$R \times 10^{40}$, cgs[a]
1	(+)-2-Methylenebenznorbornene	B_{2u}	Calcd	275	0.004	0.002	0.1
			Exptl	265			Small positive[b]
1	(+)-2-Methylenebenznorbornene	B_{1u}	Calcd	220	0.62	0.029	17
			Exptl	224	0.093	0.093	43.5[b]
2	L-5-Methylpyrrolidone	N-V₁	Calcd			0.30	7
			Exptl	190	0.25	0.25	9.7[c]
3	2,5′-Anhydro-2′,3′,-O-isopropylideneuridine	B_{2u}	Calcd (boat)	285	0.059	0.011	−2
			Calcd (chair)	285	0.059	0.011	1
			Exptl	268			1.8[d]
4	5′,6-Anhydro-2′,3′-O-isopropylidene-6-hydroxyuridine	B_{2u}	Calcd (boat)	258	0.37	0.25	−5
			Calcd (chair)	258	0.37	0.25	11
			Exptl	266	0.28	0.28	38.5[e]
5	O²-3′-Cyclouridine	B_{2u}	Calcd	285	0.059	0.011	2
			Exptl				Positive[f]
6	O²-2′-Cyclouridine	B_{2u}	Calcd	285	0.059	0.011	−0.9
			Exptl	270	0.046	0.046	−0.9[d]

[a] $f(r)$ and $f(\nabla)$ designate oscillator strength as calculated from the distance and gradient operators. Experimental oscillator strengths are obtained from $f_i = 7.67 \times 10^{-2}(\epsilon_i\, \Delta_i/\lambda_i^2)$ and rotational strengths from $R = 1.23 \times 10^{-42}(\theta_i\Delta_i/\lambda_i)$, where ϵ_i is the molar extinction maxima, θ_i is the molar ellipticity at the extremum, λ_i is the wavelength of the *i*th extremum, and Δ_i is the half band width at ϵ_i/e or θ_i/e. [b] See ref 22. [c] See ref 27. [d] See D. W. Miles, M. J. Robins, R. K. Robins, M. W. Winkley, and H. Eyring, *J. Amer. Chem. Soc.*, **91**, 824 (1969). [e] D. W. Miles, W. H. Inskeep, M. J. Robins, M. W. Winkley, R. K. Robins, and H. Eyring, *ibid*, **91**, 3872 (1969). [f] W. H. Inskeep, D. W. Miles, and H. Eyring, unpublished data.

cause considerable cancellation when the summation is performed.)

Thus, with these treatments of the chromophore and vicinal group, the final expression for the bond–bond coupling rotational strength is

$$R_a = \sum_i \sum_j \frac{2\pi}{hc} \frac{\nu_a \nu_0}{(\nu_b^2 - \nu_a^2)} \mu_{ia}^2 \mu_{jb}^2 G F_{ij} \tag{10}$$

for the transition 0 → a in the chromophore.

It is clear that the Kirkwood–Tinoco equation could have been used directly, but the approach chosen here emphasizes the empirical nature of an appeal to polarizabilities. The integrity of the calculation will be increased by a better quantum mechanical treatment of the vicinal group, or by more extensive far-uv studies, either of which gives μ_{jb} and ν_b directly, rather than by better experimental estimates of polarizability anisotropies. It should be noted that for the C–C bond the effective μ_{jb} is only greater than the value calculated by Simpson for the 133-nm transition by a factor of 1.7, and that the frequencies are the same.

Since there are no X-ray data available on the molecules for which calculations are done, all geometries were estimated from Dreiding models with occasional corrections when portions of the molecule have been determined precisely.

II. Applications

The structural formulas of the molecules to be considered here are shown in Figure 1. Table III summarizes the data and calculation results.

(+)-2-Methylenebenznorbornene (1). Optical activity arises chiefly from two mechanisms known as the coupled oscillator effect and the one-electron effect. The first mechanism may be large when electronic transition moments are large in both the chromophore and vicinal group, with a small separation in energy. The second mechanism becomes large when electric transition moments in the chromophore are large and when the vicinal group possesses a strong asymmetric static field to perturb the chromophore's molecular orbitals. In compound **1** the ethylenic and benzene substituents are in close proximity and both contain intense electronic transitions with close-lying energies, and a strong coupled oscillator contribution to the rotational strength of any of the observed near-uv transitions is expected. On the other hand the near symmetry of the molecule reduces the asymmetric static field essentially to that stemming from the 2-methylene substituent, which is not a particularly strong force field. Thus, it is a safe *a priori* conclusion that a coupled oscillator calculation should explain the observable CD spectra of this molecule.

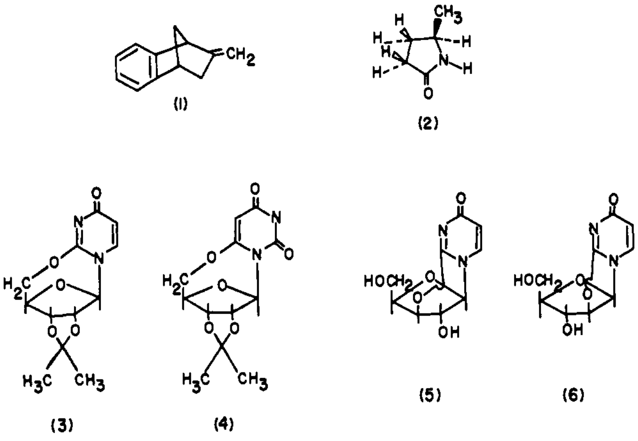

Figure 1. Structures of the example molecules considered.

Sandman and Mislow[22] have presented the CD, ORD, and absorption spectra of **1**. They reported rotational strengths of -20×10^{-40} cgs at 207 nm

---

(22) D. J. Sandman and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 645 (1969).

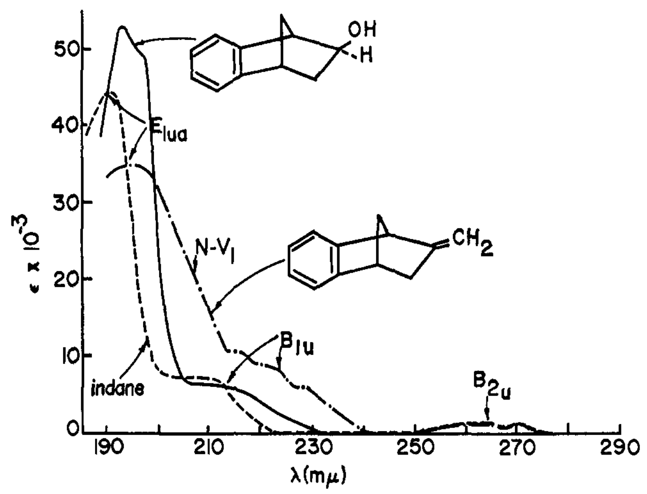

Figure 2. The uv spectra of indan, (+)-*exo*-2-benznorbornene, and (+)-2-methylenebenznorbornene (**1**). The incorporation of the ethylenic chromophore is estimated from the absorption data to reduce the E_{1ua} oscillator strength by at least 0.3. A corresponding increase must take place in the ethylenic N–V_1 transition at 207 nm, which would approximately double the oscillator strength of this transition in relation to its value in the isolated ethylenic chromophore.

and 43.5 × 10^{-40} cgs at 224 nm with a smaller positive Cotton effect at 260 nm. The origin of the two long-wavelength Cotton effects was attributed to the B_{2u} and B_{1u} transitions of benzene, and it was tentatively suggested that the negative Cotton effect at 207 nm arises from the ethylenic N–V_1 transition. The truth of this latter suggestion is strongly indicated by a comparison of the absorption spectra of **1**, indane, and (+)-*exo*-2-benznorbornenol, Figure 2. In the region of the E_{1ua} band of benzene (around 190 nm) it is seen that **1** displays a substantially reduced extinction and a broadening on the red side in contrast to the other two. In all three molecules the structural features of the benzoidal moiety and its immediate neighborhood are too similar to explain these differences, particularly the loss of extinction. The absorption spectra of (+)-*exo*-2-benznorbornenol (Figure 2) and (+)-(1*S*)-2-methylenebicyclol[2.2.1]heptane[22] place the E_{1ua} band of the isolated benzene nucleus of compound **1** at about 193 nm and the N–V_1 band of the isolated ethylenic chromophore at 195 nm, respectively.

Again using the expectation of a small static field, one can calculate the changes in oscillator strength of the ethylenic band of compound **1**, f_{coupled}, to that in (+)-(1*S*)-2-methylenebicyclo[2.2.1]heptane,[23] f_{isolated}, by the expression[24]

$$1 - \frac{f_{\text{coupled}}}{f_{\text{isolated}}} = \frac{4}{h\nu_a\mu_a^2}\sum_b \frac{\nu_a\nu_b}{\nu_b^2 - \nu_a^2} V_{a,b}\vec{\mu}_a \cdot \vec{\mu}_b \qquad (11)$$

where a designates the N–V_1 band and b the E_{1ua} band. Other benzene transitions, of course, also contribute to the total change in oscillator strength of the ethylenic band but would probably contribute much less because of the greater energy differences involved. When the interaction potential, $V_{a,b}$ is calculated in precisely the same manner as in rotational strength calculations

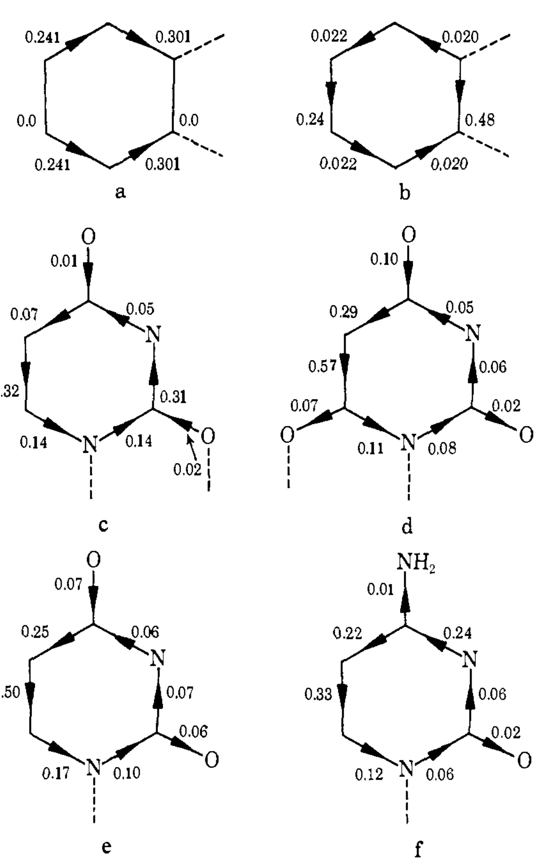

Figure 3. The P_{rs} values of the chromophores considered: a and b are the B_{2u} and B_{1u} transitions of the chromophore in **1**; c, the B_{2u} transition of the chromophore in **4**, **6**, and **7**; d, the B_{2u} transition in **5**; e and f, the B_{2u} transitions in uracil and cytosine.

(*i.e.*, by bond–bond dipole coupling), the oscillator strength of the N–V_1 transition is found to increase by a factor of 2.4 over its isolated value of 0.3 (a likely lower limit).[25] The corrected oscillator strength, 0.73, then provides an estimate of the magnitude of the transition moment along the ethylene bond by the relation

$$\mu_{jb} = \frac{f_{\text{coupled}}}{4.703 \times 10^{29}\bar{\nu}_b}$$

and this value was used in the calculation of B_{2u} and B_{1u} rotational strengths (see below). The total value of the interaction potential used in eq 11 is 0.4 eV, which gives a rough estimate of the spectral shift of the N–V_1 transition from 195 to 207 mμ. Thus the loss of extinction (hypochromism) in the 190–200-mμ spectral region, and the broad new absorption above 200 mμ displayed by compound **1** relative to (+)-*exo*-2-benznorbornenol, is found to arise from the strong dipole–dipole interaction between the two near-degenerate transitions, shifting the N–V_1 band to the red and the E_{1ua} band to the blue, with the N–V_1 band acquiring intensity at the expense of the E_{1ua} band. Further, results of Table III show the B_{2u} and B_{1u} transitions couple with the N–V_1 transition to give positive Cotton effects. Hence the N–V_1 transition would of necessity acquire negative contributions to its Cotton effect from these benzene transitions, which helps explain the negative Cotton effect at

---

(23) L. S. Forster, A. Moscowitz, J. G. Berger, and K. Mislow, *J. Amer. Chem. Soc.*, **84**, 4353 (1962).

(24) H. DeVoe and I. Tinoco, Jr., *J. Mol. Biol.*, **4**, 518 (1962).

(25) W. J. Potts, *J. Chem. Phys.*, **23**, 65 (1955).

207 mμ. However, theoretical and experimental results extended to the far-uv are needed for an unequivocal decision on this point. Our objective in this paper is limited to a theoretical study of the B_{2u} and B_{1u} rotational strengths.

The uv spectra of **1**, indan, *o*-xylene, and *o*-dichlorobenzene are so similar that it is likely the MO's are also similar. Thus, we have used MO's for **1** given by the Adams and Miller calculation[15] on *o*-dichlorobenzene. This procedure gives good results for chlorobenzene and toluene, as well as for the disubstituted molecules. The observed red shifts from the benzene spectrum are faithfully calculated, and the resulting B_{2u} P_{rs} values (Figure 3) show good agreement with those obtained from a Hückel-type calculation using Wohl's[26] parameters for the methyl substituents. The calculated R of the B_{2u} and B_{1u} bands agree well with experimental values (see Table III).

L-5-Methylpyrrolidone (2). The CD and absorption spectra of this molecule have been extensively studied by Urry,[27] with particular attention paid to the n-π* transition. We wish to focus attention on the π-π* transition which occurs at 190 nm for **2**. For transitions directed along bonds this molecule will have the geometric factors given in Figure 4.

For the peptide chromophore, the P_{ij} values are obtained from the molecular orbitals of Nagakura[28]

$$\psi_0 = 0.811\phi_N + 0.102\phi_C - 0.576\phi_O$$

$$\psi_a = 0.433\phi_N + 0.560\phi_C + 0.707\phi_O$$

which result in $P_{C,O} = 0.710$, $P_{C,N} = 0.516$. Excellent agreement with experiment results is obtained, as seen in Table III.

The Cyclouridines. The CD spectra of the cyclouridines are typical for nucleosides, and solvent studies supported by MO calculations indicate the ellipticity and extinction extrema result from π-π* transitions. Thus these transitions are designated as B_{2u}, B_{1u}, E_{1ua}, and E_{1ub} in the order of increasing energy (analogous to benzene, but with no implication as to MO symmetry properties). We consider only the B_{2u} transitions, since the MO's are obtained from the Pariser-Parr-Pople program of Adams and Miller[15] which includes only single-electron excitations in the configuration interaction. The resulting P_{rs} values are shown in Figure 3 including those obtained for uracil and cytosine for comparison. The difference in the cyclouridine chromophore and uracil suggests why it is difficult to draw conclusions about uridine conformation from cyclouridine data.

First, we consider the 2-5′ and 6-5′ cyclouridine examples, **3** and **4**, since the tying of the chromophore at the 5′ position eliminates some of the conformational degrees of freedom in the vicinal group. However, we must still contend with the possibility that these two molecules may have the vicinal ring oxygen atoms at the ends of either "boat" or "chair" conformations. In Table III we give the results for boat and chair conformations, and the value of the chair conformation is closer to that of the experimentally observed rotational strength in both cases (which agrees with the supposition that the chair conformer is the more stable).

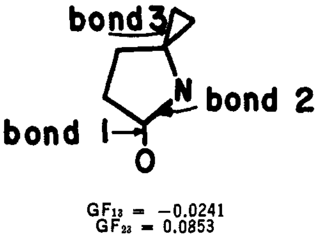

Figure 4. The geometric factors of molecule **2**.

O^2-3′-Cyclouridine (**5**) can have only one sugar-ring conformation. The three staggered positions of the O5′-C5′ bond have been described relative to the O1′-C4′ and C4′-C3′ bonds, respectively, as *gauche-gauche* (*gg*), *gauche-trans* (*gt*), and *trans-gauche* (*tg*).[29] These three conformations give rotational strengths of 1.5, 2.9, and 0.2 (× 10^{-40} cgs), respectively. For each position of O5′, the positions of H5′ must be varied. The contributions of the H5′-O5′ bond to the rotational strength range from 3.01 to −2.94, 0.92 to −0.45, and 0.96 to −0.60 (× 10^{-40} cgs), for *gg*, *gt*, and *tg*, and *tg* O5′ positions, respectively. If it is assumed that the staggered hydrogen positions are preferred with equal weightings, the corresponding contributions to the rotational strength for the three cases will be $^1/_3(-2.05 + 1.04 + 2.29) \times 10^{-40} = 0.46 \times 10^{-40}$ (*gg*), $^1/_3(0.06 + 0.15 - 0.14) \times 10^{-40} = 0.02 \times 10^{-40}$ (*gt*), and $^1/_3(-0.04 + 0.87 + 0.10) \times 10^{-40} = 0.34 \times 10^{-40}$ (*tg*). The H3′-O3′ bond under the same assumptions contributes $^1/_3(-0.21 - 0.44 + 0.62) \times 10^{-40} = 0.01 \times 10^{-40}$ cgs and is insignificant. Taking a direct average results in a rotational strength of 1.8×10^{-40} cgs (compared with 1.5×10^{-40} cgs if the hydrogen-oxygen bonds were completely omitted).

O^2-2′-Cyclouridine (**6**) possesses many possible sugar-ring conformations, but X-ray studies[30] have shown that the 3′-*exo* conformation is the more stable in crystals, and it is assumed to be the more stable in solution also. Without hydrogen-oxygen bonds, the rotational strengths are calculated to be −0.53, −0.47, and −1.86 (×10^{-40} cgs) for *gg*, *gt*, and *tg* O5′ conformations, respectively. The H3′-O3′ bond contributes $^1/_3(+0.23 + 0.27 - 0.28) \times 10^{-40} = +0.08 \times 10^{-40}$ cgs. H5′-O5′ has the ranges 0.32 to −1.39, 0.30 to −0.61, and 0.50 to −0.01, with average staggered contributions of $^1/_3(0.32 + 0.14 - 1.39) = -0.93$, $^1/_3(0.21 + 1.30 - 0.61) = 0.03$, and $^1/_3(-0.01 + 0.50 + 0.33) = 0.27$ (all × 10^{-40} cgs) for *gg*, *gt*, and *tg* O5′ positions, respectively. Taking the average over all the possibilities then gives a value of -0.9×10^{-40} cgs for the calculated rotational strength of this molecule.

III. Conclusions

The preceding examples have demonstrated that the coupled oscillator mechanism can account for a good measure of the optical activity observed in the nucleosides. Example **1** has shown that the calculations we

---

[26] A. J. Wohl, *Tetrahedron*, 24, 6889 (1968).

[27] D. W. Urry, *Ann. Rev. Phys. Chem.*, 19, 477 (1968).

[28] S. Nagakura, *Bull. Chem. Soc. Jap.*, 25, 164 (1952).

[29] M. Sudaralingam and L. H. Jenson, *J. Mol. Biol.*, 13, 930 (1965).

[30] D. M. Brown, W. Cochran, E. H. Medlin, and S. Varadarajan, *J. Chem. Soc.*, 868 (1957).

have presented do give realistic coupled oscillator results. Example 2 demonstrates that a transition moment directed along a saturated carbon–carbon bond can couple with π-electron transitions in a chromophore to a sufficient degree to explain much of the origin of the observed rotational strength, and cannot possibly be construed to be a minor effect. Then it is seen that this method of calculation can also be used to interpret the B_{2u} band in the CD spectra of the cyclouridines. The detailed effects of the hydrogen–oxygen bonds have shown that they can be safely ignored only when the resulting calculated rotational strength is sufficently strong (*i.e.*, an absolute magnitude greater then 1×10^{-40} cgs), and when this condition is not met, great care must be taken in the choice of molecular conformation.

If we consider the nucleosides in particular, there are a number of alterations in the calculation which may improve reliability, but which do not change the overall procedure. First, the molecular orbitals in the chromophore may have substantial room for improvement, particularly since any closed shell Hartree–Fock-type procedure is not very reliable in giving excited state MO's. Furthermore, the Adams–Miller calculation employed here includes only single-electron excited states, and it is widely believed that two-electron excitations contribute significantly to transition moment calculations (although the gradient method of calculation tends to minimize the effect).[31] Inclusion of these latter states in the configuration interaction might well allow a better estimation of the higher energy band rotational strengths than have been obtained thus far. As to the vicinal group, better overall geometries are needed, and an alternative to a dependency on polarizability-based parameters should be developed. Work is in progress to check some of these various possibilities. Our results show, nevertheless, that bond–bond coupling offers a useful description of the electronic–optical properties of the nucleosides with good correlation with experiment. This is further demonstrated in a companion paper which follows, where several vicinal groups are attached to the uracil and cytosine chromophores, occasionally differing by only a single bond.

Finally, it should be noted that if this were the only optical activity calculation available, the absolute configuration of all of the examples considered would have been correctly assigned!

Acknowledgment. The authors wish to thank Dr. K. Mislow for providing the uv spectra of (+)-*exo*-2-benznorbornenol. We again owe a debt of gratitude to Dr. O. W. Adams for supplying us with the latest version of his PPP program, and to Dr. R. K. Robins who supplied three of the cyclonucleosides. This work was supported by the National Institutes of Health Grant No. GM 12862-05 and the Petroleum Research Fund Grant No. PRF 253-C.

---

[31] A. J. McHugh and M. Gouterman, *Theor. Chim. Acta*, 13, 249 (1969).

Circular Dichroism of Nucleoside Derivatives. IX. Vicinal Effects on the Circular Dichroism of Pyrimidine Nucleosides[1]

Daniel W. Miles, Warren H. Inskeep, Morris J. Robins, Michael W. Winkley, Roland K. Robins, and Henry Eyring

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received October 10, 1969*

Abstract: The circular dichroism data on 38 pyrimidine nucleosides, selected to provide a basis for a reliable index of furanose conformation as a function of its optical activity, are presented. The functional dependency of the B_{2u} Cotton effect on the sugar-base torsion angle and on the specific pentose conformation is determined from theory and compared with experimental data. The theoretical description of the rotational strength as a function of the torsion angle agrees in every respect with available experimental data. Substituent effects on the signed magnitudes of the B_{2u} rotational strength generally correlate quite well with theoretical expectations. The success of the theoretical calculations depend on giving up the Kirkwood–Tinoco coupled oscillator scheme where the transition moment vector is located at the center of gravity of the chromophore and, instead, breaking down the electric transition moment into bond contributions.

In paper VIII of this series,[1] it was shown that an analysis of the $\pi \rightarrow \pi^*$ Cotton effects of cyclopyrimidine nucleosides and several other rigid systems predicts their absolute stereochemical configuration. The method of analysis is an extension of the classical coupled oscillator theory of optical activity of Kuhn,[2] which was reformulated in quantum mechanical terms by Kirkwood.[3] The method resolves the gradient version of the transition dipole moment vector into bond contributions and couples each chromophoric bond component with the far-uv transitions of the vicinal bonds by their dipole–dipole interactions. The totality of the bands in the vicinal bonds are represented by an effective transition moment with the direction of the principle polarizability of the bond

---

[1] Part VIII: W. H. Inskeep, D. W. Miles, and H. Eyring, *J. Amer. Chem. Soc.*, 92, 3866 (1969).

[2] W. Kuhn, *Trans. Faraday Soc.*, 26, 293 (1930).

[3] J. G. Kirkwood, *J. Chem. Phys.*, 5, 479 (1937).