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$\Delta H^\circ_{\rm polarizn}$ = 4 kcal/mol, a reasonable value for this system, in eq 1 again yields $\Delta H^\circ_{\rm res,6-4}$ = 6 kcal/mol. In comparison, Herndon's resonance value is 8 kcal/mol, in good agreement.[5]

Deprotonation of toluene/1-methylnaphthalene occurs on the methyl group and therefore does not involve the ring directly. However, the resulting sp^2 lone pair in the anion perturbs the ring π system. This should be more unfavorable when the perturbed system is the stable aromatic 6-electron system and less destabilizing when it is a 4-membered conjugated system. Therefore, here again the π effect of annelation is favorable and adds to polarization, leading to a fairly large $\Delta H^\circ_{\rm anneln}$ = 8.6 kcal/mol.

Finally, azulene cannot be directly compared to any one ring system, since it does not have an sp^3 carbon as the five-membered or seven-membered "constituents", cyclopentadiene and cycloheptatriene.[10] However, it is noted that its acidity is greatly increased, by 26 kcal/mol, over that of naphthalene. The increased acidity suggests a special stabilization of the azulenide anion. We note that the five-membered ring in azulene formally possess 5 π electrons. The AM1 charge densities pattern in azulene and its most stable anion, see Table II, show that deprotonation of the seven-membered ring creates a lone pair and adds a negative-charge center that helps in pushing extra electron density to the five-membered ring and forming a "quasi"-aromatic sextet. In this respect, deprotonation is analogous with protonation on the seven-membered ring that forms a tropylium-like sextet. The analogy is enhanced by the observation that the proton affinity of azulene is also larger than that of naphthalene by 25 kcal/mol, similar to the acidity difference.

Summary

In summary, compounds where deprotonation or protonation does not involve π effects give a consistent 6 ± 1 kcal/mol for charge stabilization by polarization of an annelated ring. This adds to electronic effects when deprotonation or protonation also contributes or removes π electrons. Specifically, we observe cases where annelation transfers the effects from involving a 6-electron π system to involving an annelated 4-electron system. These results, involving anions and cations, give a consistent 6 ± 1 kcal/mol for the difference between the aromatic stabilization of a first 6-electron or a second, annelated 4-electron system.

Registry No. 1, 91-20-3; **3**, 120-12-7; **6**, 90-12-0; **7**, 91-22-5; **10**, 260-94-6; **15**, 91-19-0; **18**, 542-92-7; **19**, 95-13-6; **20**, 544-25-2; **21**, 275-51-4; **27**, 120-72-9.

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[10] AM1 overestimated the heat of formation of neutral azulene by 12 kcal/mol.

Circular Dichroism of Oxiranes: An Independent Systems/Perturbation Approach

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Abstract: The circular dichroism (CD) spectra of the first two Rydberg transitions of alkyl-substituted oxiranes are interpreted by an independent systems/perturbation approach. When alkyloxirane compounds are treated as an achiral oxirane ring perturbed by alkyl substituents, quantitative relationships between CD and oxirane structure are obtained. The dipolar coupled-oscillator model of Kirkwood and Kuhn proves to be the only significant mechanism for both the n(0) → 3s and n(0) → 3p transitions. The static coupling model suggested by Gedanken et al. to account for the sign of the n(0) → 3s transition does not account for the variation in CD magnitudes that is observed.

I. Introduction

Chiral oxiranes have excited much interest in recent times because of their potential as building blocks for asymmetric synthesis.[1] They can be synthesized with high stereoselectivity from naturally occurring chiral compounds such as diethyl tartrate,[2] amino acids,[1,3] and diols,[4] or alternatively racemic mixtures can be synthesized from prochiral systems and then separated (e.g. by chromatography[5]). The stereochemistry of an oxirane can often be determined from knowledge of the synthetic route or on the basis of packing arguments. An independent verification of the assignment is desirable, especially for systems with similar substituents on C2 and C3 in Figure 1. The circular dichroism (CD) experiments of Gedanken et al.[6-8] potentially fill this role since the sign and magnitude of a CD band is directly related to its stereochemistry. If the mechanism giving rise to the CD is understood, then the stereochemistry of the system can be determined from the observed spectrum.

Gedanken et al.[6-8] have measured the CD of a number of oxiranes in the region of 185–155 nm. Two of the low-lying transitions have been assigned as Rydberg transitions from a nonbonding $2p_x$-type orbital largely localized on the oxygen of the oxirane ring to the oxygen 3s and 3p states.[9] In accord with ref 9, we shall denote these transitions as n(0) → 3s and 3p, respectively. The n(0) → 3s transition is separated from its neighboring transitions, and the CD band signs reflect the positions of the substituents according to a quadrant rule,[7] showing a positive CD for substituents with $y > 0$ and $x > 0$ or with $y < 0$ and $x < 0$ (cf. Figure 1) and a negative CD in the other two quadrants. This behavior is precisely what is expected on symmetry grounds (without any reference to mechanism) for an approximately C_{2v} oxirane in the presence of substituents on C2 and C3 oriented as in Figure 1. In order to understand more complicated CD variations as a function of substituent, it is necessary to determine what mechanism is the dominant contributor to the CD. Gedanken et al.[7] have suggested that the sign variations can be rationalized with Schellman's symmetry analysis[10] of the one-

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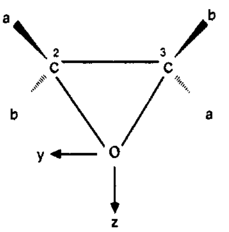

Figure 1. Structure of oxiranes illustrating axis system used.

electron or static coupling model of Condon et al.[11] However, the n(0) → 3s transition is electric dipole allowed (eda), so the coupled oscillator model of Kirkwood and Kuhn (CO)[12] is almost certainly dominant over any other mechanism. The justification of this statement lies in mechanistic arguments, which have themselves been verified by many CD studies on eda transitions (see e.g. ref 13–15). We shall return to this below. Thus, any analysis based on the static coupling model is inapplicable. The n(0) → 3p Rydberg transition is not as well separated from its neighbors as the n(0) → 3s transition, and no clear empirical relationship between band sign and stereochemistry has yet emerged. It is the aim of this work to understand the CD of the n(0) → 3s and n(0) → 3p Rydberg transitions in oxiranes by comparing theoretical predictions with the observed CD.

II. Independent Systems/Perturbation Approach to CD

Both the n(0) → 3s and 3p transitions are essentially localized within the achiral oxirane ring so the CD results from chiral perturbation by the ring substituents. Under such circumstances the most profitable approach for gaining an understanding of the observed CD has proved to be the independent systems/perturbation (ISP) approach.[16-21] In this approach perturbation theory is used to express the CD in terms of the electrostatic interaction of the achiral ring (A) with the ring substituents that form the chiral perturbation and are divided into a set of chromophoric subunits (C). The different terms in the perturbation expansion correspond to mechanisms such as the static coupling mechanisms[11] and dynamic coupling mechanisms[16] (first-order mechanisms), the coupled-oscillator mechanism[12] (first-order mechanism for electric dipole allowed transitions), and the various second-order mechanisms.[17,21] When the electrostatic interaction is expanded in a multiple series, each of these mechanisms becomes a sum of terms involving different multipole moments and different r_c^{-n} factors, where r_c is the distance between the A and C origins and n is a positive integer. Because the multipole expansion converges at about van der Waals radii and r_c is generally two or more bond lengths, the value of n is a significant determiner of the relative magnitudes of the terms since r_c^{-n} decreases dramatically with increasing n. If other parts of a term are not zero by symmetry or geometry, it is likely that the term with smallest n value, i.e. for eda transitions the CO term which is r_c^{-2} dependent, is dominant. The CO vanishes only for magnetic dipole allowed transitions and certain special geometries, which prove not to be relevant here. Thus, the CO dominates for the n(0) → 3s transition and two components of the n(0) → 3p. The n(0) → $3p_y$ transition is magnetic dipole allowed; thus, the CO vanishes. The largest mechanisms for magnetic dipole allowed transitions are r_c^{-3}, and in fact A_2 magnetic dipole allowed transitions in oxiranes are r_c^{-4} as was the case for A_2 carbonyl transitions,[22] so the n(0) → $3p_y$ CD is predicted to be small compared with that of the other two components, and so not a significant contributor to the CD spectrum. We shall therefore proceed by examining the theoretical predictions of the CO for n(0) → 3s, $3p_x$, and $3p_z$ and compare the results with experiment.

Coupled-Oscillator Mechanism. The first coupled oscillator term involves the coupling of two skewed electric dipole transition moments, one on A and one on C. Pictorially, the two dipoles can be visualized as part of a helix, with the sign of the CD depending on the handedness of the helix. A quantitative expression for the CD is arrived at by using first-order perturbation theory and a dipolar electrostatic interaction between A and C. We shall quote the general expression for an arbitrary transition and then simplify it for application to the oxiranes. The CO CD strength **R** of the $|o\rangle \rightarrow |a\rangle$ transition on A when perturbed by C is[19] given in eq 1 where the summation is over all C and over

$$\mathbf{R}[|o\rangle \rightarrow |a\rangle] = -\epsilon_a(hr_c^2)^{-1}\sum_C\sum_{|c\rangle}\epsilon_c(\epsilon_c^2 - \epsilon_a^2)^{-1}\, a^{0a}a^{a0}{:}(c^{oc} - 3\rho c^{oc}\cdot\rho)\rho x c^{co} \quad (1)$$

all electric dipole allowed transition moments c^{co} from $|o\rangle \rightarrow |c\rangle$ of energy ϵ_c on C; a^{oa} is the electric dipole transition moment of the $|o\rangle \rightarrow |a\rangle$ transition on A, which occurs at energy ϵ_a; $\rho = \mathrm{r}_c/|\mathrm{r}_c| = \mathrm{r}_c/r_c$ is the unit vector along the line from the A origin to that of C; a colon implies the scalar product of two second-rank tensors.

The transitions to which we apply eq 1 are x and z polarized. For these situations eq 1 takes the forms

$$\mathbf{R}(z/\mathrm{A}_1 \text{ polarized}) = -r_c^{-2}A(\alpha^c{}_{yz}\mathrm{p}_x - \alpha^c{}_{xz}\rho_y - 3\alpha^c{}_{wy}\rho_w\rho_x\rho_z + 3\alpha^c{}_{wx}\rho_w\rho_y\rho_z) \quad (1a)$$

$$\mathbf{R}(x/\mathrm{B}_1 \text{ polarized}) = -r_c^{-2}A(\alpha^c{}_{xz}\rho_y - \alpha^c{}_{xy}\rho_z - 3\alpha^c{}_{wz}\rho_w\rho_x\rho_y + 3\alpha^c{}_{wy}\rho_w\rho_x\rho_z) \quad (1b)$$

where $A = (\epsilon_a a_w{}^{oa}\mathrm{a}_w{}^{ao}/2h)$ is the oscillator strength times transition energy divided by $2h$ for the n(0) → 3s or n(0) → 3p transition and $\alpha^c{}_{vw} = \epsilon_c(\epsilon_c{}^2 - \epsilon_a{}^2)^{-1}c_v{}^{oc}c_w{}^{co}$ is the vwth component of the dynamic polarizability of the ring substituents of the oxiranes at frequency ϵ_a. Summation over $|c\rangle$, C, and $w = (x, y, z)$ is implied. Thus, the magnitude of the CO CD is proportional to (i) the energy of the transition being studied, (ii) the oscillator strength of the transition being studied, and (iii) the inverse of the square of the distance between A and C. Each of these factors is positive. The CO CD is also related to the components of the dynamic polarizability of the substituents and the relative orientation of A and C. ρ is defined to be a unit vector connecting A and C origins so its contribution reflects how the oxirane substituents are positioned relative to A. For a simple sector rule to be operative ρ components must be the only factors in eq 1a and 1b that can vary in sign. This is not the case since the α_c components vary as a function of the orientation of the transition moments in each C and can be positive or negative. This is discussed further in section III and has been previously noted by Weigang.[15]

Equations 1a and 1b can therefore be parametrized from the normal absorption spectrum, the geometry of the system, and an estimate of the dynamic polarizability of the perturbing units (C). $a_w{}^{oa}a_w{}^{a0}$ is the oscillator strength of the transition of interest, and ϵ_a is its transition energy. $\rho = (\rho_x, \rho_y, \rho_z)$ and r_c are, respectively, the orientation and length of a line connecting the A origin to that of C. The A origin is approximately the oxygen atom, and we shall place the origins of the (C) chromophores to be at the carbon atoms, which reflects the electron density and means that each C–C bond notionally makes two contributions to the CO CD. (This choice results from the way we parametrize the polarizability.) Finally, $\alpha^c{}_{vw}$ is the vwth component of the dynamic polarizability of a C unit. The signs and *relative* magnitudes of the components of α_c for alkyl C can be determined from the geometry of the system if we make the assumption that transitions along the C–C bonds make a more significant contribution than those perpendicular to the C–C bonds. Since C–C bond polarizabilities do not vary significantly from alkyl group to alkyl group, we can

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determine relative CD strengths for a series of compounds and so make comparisons with experiment. For convenience we shall take the polarizability to be of unit magnitude for the remainder of this work.

III. n(0) → 3s Oxirane Transition

The semiquantitative application of eq 1 to the n(0) → 3s transition is relatively straightforward in light of the discussion of the preceding section. We begin by noting that the n(0) → 3s transition is polarized out of the oxirane plane and so eq 1b is appropriate. The quadrant geometry dependence, observed by Gedanken et al.[7] and discussed in the Introduction, follows directly from eq 1b, as symmetry requires it must. However, it should be noted that eq 1b indicates that the sign oscillation is the result of both the *position* and *orientation* of the substituents, not simply position as previously assumed.[7] Thus, two chromophores in the same quadrant, but with different orientations, may have canceling, rather than reinforcing, contributions to the CD. This factor becomes relevant for the relative contributions of alkyl groups of different lengths and sizes as we shall see below. A simple purely geometry-dependent sector rule is therefore not appropriate for eda transitions, in contrast to the situation for many magnetic dipole allowed transitions, such as the n → π* transition in carbonyl compounds.[22]

A purely position-dependent model such as the static coupling model, which has previously been suggested to account for the geometry dependence of the CD, cannot account for the details of the observed behavior since it predicts a simple increase in CD magnitude with increasing number of carbons in the alkyl substituent, contrary to the experimental data. The expression for the static coupling CD strength ($\mathbf{R}_{\text{s-c}}$) of order r_c^{-3} for an electric dipole allowed transition[13] illustrates this point clearly (eq 2) where

$$\mathbf{R}_{\text{s-c}} = -{}^{3}\!/_{2} r_c^{-3} \mu_A \cdot \boldsymbol{m}_A Q_{A_{xy}} q_c \rho_x \rho_y \qquad (2)$$

state labels and energy denominators have been omitted for clarity, summation over all chromophores C is implied, q_c is the charge of C, μ_A is the electric dipole transition moment on A. $\mathbf{m}_A$ is the magnetic dipole transition moment on A, and $Q_{A_{xy}}$ is the xy component of the quadrupole transition moment on A. The sign of the CD described by eq 2 depends on the position of the substituents and is independent of their orientation. (In fact eq 2 strictly vanishes for uncharged C, so, in order to be considered applicable to alkyl systems, each C must be further divided into charged subunits, which is not really in accord with the chromophoric approach from which this equation is derived. Higher order nonvanishing static coupling terms do not have the simple quadrant geometry dependence of eq 2 and are even smaller compared with the coupled oscillator term of eq 1, being at best r_c^{-4} dependent.)

In order to make semiquantitative predictions of the n(0) → 3s CD using the CO CD of eq 1b, we need the geometry of the system. For convenience we shall use the approximate oxirane geometry with all C–C and C–O bonds of length 1 unit, a C–O–C angle of 60°, and angles between the first substituent C–C bond ($\mathbf{b}_1$ in Figure 2) and the ring bonds being the tetrahedral angle τ. These approximations should not affect the results significantly. Because of the way we have chosen to parametrize the polarizability of an alkyl substituent (see above), we can determined the CO CD for successive bonds along the chain beginning with that closest to the oxirane ring and then add the contributions together to determine an estimate of the total CD. The coupled-oscillator contribution to the CD of the n(0) → 3s CD arising from the first C–C bond of an *S* substituent can be determined as follows. (That for an *R* substituent is opposite in sign and of the same magnitude.) The C–C bond lies along $\mathbf{b}_1 = (\sin(\tau/2), (3/4)^{1/2} \cos(\tau/2), -1/2 \cos(\tau/2))$ (cf. Figure 2), $\alpha^c/|\alpha^c| = -\mathbf{b}_1\mathbf{b}_1$, the first carbon atom lies at the end of $\mathbf{b}_0 = (0, 1/2, -(3/4)^{1/2}) = \mathbf{r}_{c1} = r_{c1}\rho_{c1}$, and the second lies at the end of $(\mathbf{b}_0 + \mathbf{b}_1) = \mathbf{r}_{c2} = r_{c2}\rho_{c2}$. We shall denote A by A_s for the n(0) → 3s transition and leave A unspecified since it is a function of the oxirane. An estimate for the n(0) → 3s CD contribution from the first bond of an alkyl substituent then follows from substitution of these parameters into eq 1b and addition of the two contributions. As (*S*)-methyloxirane has only one C–C bond ($\mathbf{b}_1$) in its substituent, eq 3 should describe its CD. The

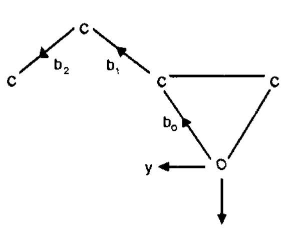

Figure 2. Geometry of (*S*)-alkyloxiranes used in the calculations.

$$\mathbf{R}(\text{n}(0) \rightarrow 3\text{s})[\mathbf{b}_1] \approx (1.52 - 0.07)A_s \approx 1.45A_s \qquad (3)$$

observed CD for the n(0) → 3s transition (*S*)-methyloxirane is a positive band[6] in accord with eq 3. The additive nature of the ISP expressions means that the CD of a dimethyloxirane should be the sum of the two single methyloxirane contributions, viz.

$$\mathbf{R}(\text{n}(0) \rightarrow 3\text{s})\ [(S,S)\text{-dimethyloxirane}] \approx 2.9A_s\ ((S,S)\text{-dimethyl})$$

If the CO expressions are an accurate description of the CD then

$$2.9A_s\ ((S,S)\text{-dimethyl})/[1.45A_s\ ((S)\text{-methyl})]$$

should equal the ratio of the observed CD strengths. Now the oscillator strengths of the n(0) → 3s transition in these two compounds appear to be of similar magnitude,[6] so the observed CD in (*S,S*)-dimethyloxirane should be approximately twice that of (*S*)-methyloxirane. Although cancellation effects from neighboring bands affect the magnitude of the observed peaks, the experimental data summarized in Table I confirm this prediction, thus supporting the applicability of eq 1b.

The next step is to determine the CO CD contribution from a second C–C bond ($\mathbf{b}_2$), whose coordinates are $\mathbf{b}_2 = (-\cos\tau \sin(\tau/2) + \sin\tau \cos(\tau/2) \sin\theta, -(3/4)^{1/2} \cos\tau \cos(\tau/2) + 1/2 \sin\tau \cos\theta - (3/4)^{1/2} \sin\tau \sin(\tau/2) \sin\theta, 1/2 \cos\tau \cos(\tau/2) + (3/4)^{1/2} \sin\tau \cos\theta + 1/2 \sin\tau \sin(\tau/2) \sin\theta)$, where θ is the angle of $\mathbf{b}_2$ about $\mathbf{b}_1$, the first C–C bond (see Figure 2). The two relevant carbon atoms lie at the ends of $\mathbf{r}_{c2}$ and $\mathbf{r}_{c3} = \mathbf{r}_{c2} + \mathbf{b}_2$. Upon substitution into eq 1b and performance of a rotational average (assuming free rotation) with respect to θ,[23] we find eq 4. $\mathbf{R}[\mathbf{b}_2]$ is thus of opposite sign from $\mathbf{R}[\mathbf{b}_1]$, and about 15% of its magnitude, so an ethyl-substituted oxirane is predicted to have a smaller n(0) → 3s CD than a methyl-substituted oxirane, as is observed. Succeeding C–C bonds become increasingly more difficult to treat quantitatively due to (possibly hindered) rotation about more than one bond. The contribution from the first C–C bond is likely to be the dominant one due to the dependence of the CD contribution on distance from the oxygen. Thus, the sign of the n(0) → 3s CD will be positive for an (*S*)-alkyl substituent and negative for an (*R*)-alkyl substituent. The CD induced by non-alkyl substituents whose dominant transitions are not polarized along $\mathbf{b}_1$, $\mathbf{b}_2$, etc., must be determined independently with the same principles as we have used for alkyl systems.

$$\mathbf{R}(\text{n}(0) \rightarrow 3\text{s})[\mathbf{b}_2] \approx (-0.186 - 0.036)A_s \approx -0.22A_s \qquad (4)$$

Equations 3 and 4 are sufficient to enable semiquantitative predictions for the n(0) → 3s of a range of compounds. The fourth column of Table I gives calculated values of $\Delta\epsilon/A_s$. Now since A_s is oscillator strength times transition energy divided by $2h$, in order to compare theory with experiment, we should compare the product of columns 1 and 3 with column 2 in Table I. In doing this we are ignoring both the effect of cancellation of CD strength by neighboring transitions and the fact that theory gives total CD strength whereas the expermental data are the maximum value of $\Delta\epsilon$ from the experimental curves. Nonetheless, we can conclude that a satisfactory correspondence between theory and experiment is observed.

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[23] Rotational averaging performed by P. M. Rodger.

Table I. CD of the n(0) → 3s and n(0) → 3p Transitions of Oxiranes and Methyloxetane[a]

	n(0) → 3s				n(0) → 3p			
	exptl			theor:	exptl		theor: $\Delta c/A_p$[c]	
	ϵ_{max}	(nm)	$\Delta\epsilon_{max}$	$\Delta\epsilon/A_s$	ϵ_{max}	$\Delta\epsilon_{max}$	x-pol	z-pol
(*S*)-methyloxirane	2200	(165–178)	+14	+1.45	5500	−12	−2.71	+1.45
(*S*,*S*)-dimethyloxirane	2500	(169–180)	+23	+2.9	3800[d]	−2[d]	−5.42	+2.9
(*R*)-*tert*-butyloxirane	1000	(168–181)	−2.7	−0.79	1300[d]	−0.2[e]	+1.72	−0.79
(*S*,*S*)-methylethyloxirane	0.65[b]	(170–179)	+33[b]	+2.7	1.0[b,d]	+0.0[b,c]	−5.09	+2.7
(*S*,*R*)-methylethyloxirane	0.26[b]	(174–185)	+2.5[b]	+0.22	0.6[b]	−11.8[b]	−0.33	+0.22
(*R*)-trimethyloxirane	3.0[b]	(175–187)	−4.2[b]	−1.45	3.0[b,d]	−2.9[b,e]	+2.71	−1.45
(*R*)-[(*S*)-1-methylpropyloxirane]	2700	(167–180)	−5.0	$-x, x < 1.45$	2600[d]	+1.3[d]	$+y, y < 2.71$	$-x, x < 1.45$
(*S*)-methyloxetane	950	(180–198)	+4.5	+1.45	3400	−3.5	−2.71	+1.45

[a] Experimental data from ref 6–8 and theoretical predictions from this work. Experimental oscillator and CD strengths are values at maximum peak height; theoretical CD strengths are total CD strength. The n(0) → 3p transition is assigned with energy differences relative to the n(0) → 3s transition (see text). [b] Denotes arbitrary units that can only be used comparatively within a row of a table. [c] A is proportional to the oscillator strength of the transition (see text). [d] Denotes shoulder in normal absorption and usually corresponds to a small CD band, which may only be a trough between two larger ones. [e] CD of n(0) → 3p is of opposite sign from the number quoted because of the presence of neighboring overlapping bands of opposite sign.

IV. n(0) → 3p Oxirane Transition

In contrast to the n(0) → 3s transition, no general trends have become apparent in the CD of the n(0) → 3s transition. Consideration of the nature of the transition and the CD predictions of the ISP approach enable the spectra to be at least partly unraveled. The n(0) → 3s transition is a helpful clue in understanding the n(0) → 3p transition. Both transitions originate in n(0) and end in a Rydberg state, which is essentially localized on the oxygen of the ring and so little affected by the substituents. As a result, variations in transition energy from oxirane to oxirane will be largely due to variations in n(0), and so the same for both transitions. Now the n(0) → 3s transition is clearly identifiable in any alkyloxirane spectra (it is lowest lying), so knowledge of the n(0) → 3s and 3p energy spacing in any one compound means that the position of the n(0) → 3p transition can be approximately determined for any compound. Both transitions are clearly identifiable in (*S*)-methyloxirane, the lowest end of the n(0) → 3p transition lying about 5000 cm^{-1} higher in the energy than the lowest energy end of the n(0) → 3s transition. Cancellation effects in the CD spectrum mean that one cannot be more definitive. Previous assignments of the n(0) → 3p band have been made by assuming that it is the first significant CD peak after the n(0) → 3s transition. This method involves the implicit assumption that other transitions in the neighborhood of the n(0) → 3p transition have small oscillator and CD strengths. The two methods of assignment reach different conclusions in those compounds where this assumption appears to break down. We shall proceed by using the energy spacing assignment principle, testing it by comparison of theory with theory experiment.

Application of the energy spacing assignment principle to the spectra in ref 6–8 suggests that the n(0) → 3p CD of an (*S*)-alkyloxirane is negative (n(0) → 3s is positive), that of an (*R*)-alkyloxirane is positive, and that methyl substituents make the largest contribution to the observed CD. We now have an empirical stereochemistry/spectroscopy relationship for the n(0) → 3p transition, which is in accord with the symmetry of the oxirane chromophore. In addition, we can say that the unsystematic variation of n(0) → 3p transition energy and band sign observed by Gedanken and Schurig[8] appears to be the result of neighboring and overlapping transitions interfering with the n(0) → 3p spectrum, rather than variations in the contributions of the three component transitions to the net n(0) → 3p CD. It remains only to justify this behavior theoretically so the limits of its application can be understood. We shall proceed by determining the ISP CD for the n(0) → 3p transition.

The three n(0) → 3p component transitions and their assignments are: n(0) → 3p$_x$ (A$_1$ polarized), n(0) → 3p$_y$ (A$_2$ polarized), and n(0) → 3p$_z$ (B$_1$ polarized). The A$_1$ and B$_1$ transitions are both eda whereas the A$_2$ transition is electric dipole forbidden and mda. The A$_2$ normal absorption, which gets its intensity through vibronic coupling, will therefore be dominated by the A$_1$ and B$_1$ transitions, which have zeroth-order intensity. By way of contrast, the CD of all three transitions is due to the coupling of the oxirane chromophore with the rest of the molecule. A$_1$ and B$_1$ require an induced magnetic moment, and A$_2$ required an induced electric moment. This might suggest that the CD of the three transitions is of comparable magnitude. However, before making such a deduction, one must consider the efficacy of the mechanisms by which the required moments are induced. As for the n(0) → 3(s) transition, the *magnetic* moment required by the A$_1$ and B$_1$ transitions is dominated by the r^{-2} coupled-oscillator term. However, the largest possible contribution to an induced electric moment is an r^{-3} coupling term, and in fact the symmetry of the oxirane chromophore causes the r^{-3} terms to vanish and the largest contribution to the induced electronic moment to be an r^{-4} coupling term.[20] Thus, despite the fact that the A$_2$ CD intensity is probably larger compared with the A$_1$ and B$_1$ CD intensities than the corresponding normal absorption intensity ratios, the A$_2$ CD is almost certainly dominated by the A$_1$ and B$_1$ CD. Metal complexes provide an analogous example: the CD intensities of the eda metal–ligand charge-transfer transitions are at least 1 order of magnitude larger than the CD intensities of the mda d–d transitions. We can therefore conclude that the dominant features of the n(0) → 3p spectrum are almost certainly determined by the A$_1$ and B$_1$ components.

The CD of the n(0) → 3p$_x$ transition is given by eq 1a and that of the n(0) → 3p$_z$ transitions by eq 1b. As in section III, we begin with the CD contribution of $\mathbf{b}_1$ and $\mathbf{b}_2$ to the two transitions and then combine these to determine semiquantitative CD strengths of n(0) → 3p$_x$ and n(0) → 3p$_z$ for a number of compounds. The resulting expressions are

$$\mathbf{R}(\mathrm{n}(0) \rightarrow 3\mathrm{p}_x)[\mathbf{b}_1] \approx (-2.66 - 0.05)A_x \approx -2.71A_x$$

$$\mathbf{R}(\mathrm{n}(0) \rightarrow 3\mathrm{p}_x)[\mathbf{b}_2] \approx (0.46 - 0.13)A_x \approx 0.33A_x$$

$$\mathbf{R}(\mathrm{n}(0) \rightarrow 3\mathrm{p}_z)[\mathbf{b}_1] \approx (1.52 + 0.07)A_z \approx 1.45A_z$$

$$\mathbf{R}(\mathrm{n}(0) \rightarrow 3\mathrm{p}_z)[\mathbf{b}_2] \approx -(0.186 + 0.036)A_z \approx -0.22A_z$$

where $A_{x,z}$ is A for the n(0) → 3p$_{x,z}$ transition. The results in the final two columns of Table I follow directly.

For comparison with experiment, it is necessary to determine the relative contributions of the two transitions to the CD. This requires some estimate of their relative oscillator strengths to determine A_x/A_z. Polarized normal absorption spectra of the n(0) → 3p transition are not available, so we shall estimate approximate weightings of the n(0) → 3p$_x$ and 3p$_z$ transitions from the normal absorption and CD spectra of (*S*)-methyloxirane, whose n(0) → 3p transition is relatively isolated from the rest of the spectrum, and then apply this weighting to other compounds. This process is in accord with the ISP approach. We note that the n(0) → 3p CD of (*S*)-methyloxirane is negative and of approximately the same magnitude as that of the positive n(0) → 3s transition, thus

$$\mathbf{R}(\mathrm{n}(0) \rightarrow 3\mathrm{s}) \approx -\mathbf{R}(\mathrm{n}(0) \rightarrow 3\mathrm{p}_x) - \mathbf{R}(\mathrm{n}(0) \rightarrow 3\mathrm{p}_z)$$

so

$$1.45A_s \approx 2.71A_x - 1.45A_z$$

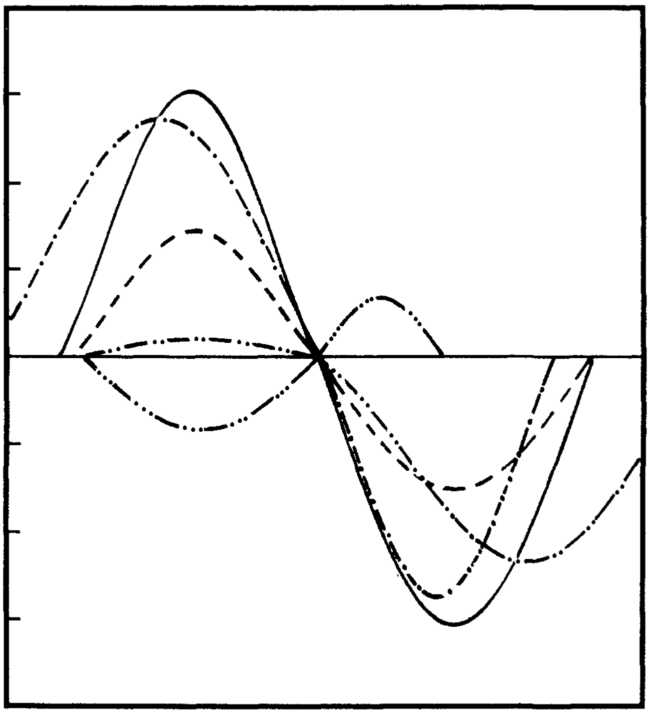

Figure 3. Predicted CD spectra of n(0) → 3s and n(0) → 3p transitions in oxiranes. The effect of neighboring transitions is ignored: (- - -) (*S*)-methyloxirane, (—) (*S*,*S*)-dimethyloxirane, (-···-) (*R*)-*tert*-butyloxirane, (-··-) (*S*,*S*)-methylethyloxirane, (-··-) (*S*,*R*)-methylethyloxirane.

Now, the n(0) → 3s oscillator strength is similar to that of the total n(0) → 3p oscillator strength so $A_s \approx A_x + A_z$. We can therefore deduce that the n(0) → 3p$_x$ transition must have an oscillator strength of approximately 2–2.5 times that of the n(0) → 3p$_z$ transition. (Since any cancellation of the CD intensity in the observed spectrum is equal and opposite for the n(0) → 3s and n(0) → 3p transitions, cancellation effects can be ignored in this approximate calculation.) The spectra that would be predicted with these deductions, assuming approximately the same oscillator strengths in the different compounds and ignoring cancellation effects, are illustrated in Figure 3.

Two major factors determine whether the theoretical predictions summarized in Figure 3 resemble the CD spectra observed. The first is that cancellation between the 3s and 3p CD bands may occur, making both bands smaller and altering the apparent ratio of their magnitudes. The second factor is the presence of other overlapping bands, which may be sufficiently strongly CD active to alter the appearance of a spectrum, particularly in the region of the n(0) → 3p transition. This second factor is of most significance for those systems where the n(0) → 3p band is not clear in the normal absorption. Further theoretical work on the normal absorption spectrum of these compounds is required to clarify the situation.

V. Conclusion

In conclusion we can say that the circular dichroism of the first two Rydberg transitions in alkyloxiranes has proved amenable to an independent systems/perturbation approach. The dipolar coupled-oscillator model proved to be an adequate description of the CD, at least on a semiquantitative level. The relationship between CD band sign and geometry observed by Gedanken et al. for the n(0) → 3s transition, viz., that an *S* substituent gives rise to a positive CD signal, has been given a sound theoretical basis, so that its limitations can be determined. In addition, the variation of n(0) → 3s CD magnitude as a function of substituent follows directly from the coupled-oscillator expressions. These variations cannot be understood with a purely position dependent model such as the static coupling model.

The n(0) → 3p transition is a little more complicated to treat theoretically since there are three component transitions. However, the p$_y$ component can be ignored to a first approximation since it is electric dipole forbidden and so will have a CD of much smaller magnitude than the other two components. The relative weighting of the p$_x$ and p$_z$ components was determined empirically from a spectrum where both the n(0) → 3s and n(0) → 3p transitions are isolated. The conclusion reached is that an *S* substituent gives rise to a net negative n(0) → 3p CD, and, as is the case for the n(0) → 3s transition, a methyl substituent is the most effective inducer. Previous attempts to collate the n(0) → 3p experimental data on a purely empirical level had foundered due to the interference caused by neighboring transitions.[8]

Thus, these Rydberg transitions do provide an alternative means of investigating the stereochemistry of oxiranes. The main problem from a practical point of view for the organic chemist is that they occur in the vaccum ultraviolet region of the spectrum and therefore require specialized experimental equipment and technique.[6-8] This work illustrates the point made by Johnson[24] that a great deal of additional information is available just beyond the range of commercial instruments. Appropriate equipment for such measurements is becoming more readily available, and for an oxirane the handedness of a system needs only be determined once for each preparation method. An alternative approach would be to create an accessible transition in an oxirane. The most obvious way to do this is to put, say, a carbonyl onto one of the ring substituents. However, if it is free to rotate, the carbonyl CD will be small and too complicated for simple empirical rules. Further consideration needs to be given to this problem. The next stage of the theoretical analysis is to extend this work to non-alkyl-substituted oxiranes. For this, consideration needs to be given to a means of approximately determining the components of the polarizability tensor of the substituents.

The results of this work should apply with equal validity to oxetane compounds (oxetanes have a four-membered ring of one oxygen and three carbons). (*S*)-2-methyloxetane was also studied by Gedanken and Schurig,[8] and the limited evidence so far available suggests that the analysis of the oxiranes can be transferred directly to the oxetane compounds. In fact the bands in (*S*)-methyloxetane are more clearly separated than in the oxirane analogue, so the oxetane situation will probably be easier to deal with than the oxiranes.

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Registry No. (*S*)-Methyloxirane, 16088-62-3; (*S*,*S*)-dimethyloxirane, 63864-69-7; (*R*)-*tert*-butyloxirane, 41796-67-2; (*S*,*S*)-methylethyloxirane, 93132-82-2; (*S*,*R*)-methylethyloxirane, 93132-83-3; (*R*)-trimethyloxirane, 70355-44-1; (*R*)-[(*S*)-1-methylpropyloxirane], 70640-56-1; (*S*)-methyloxetane, 75492-29-4.

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[24] Johnson, W. C., Jr. Proceedings of NATO Advanced Study Institute in Polarized Spectroscopy of Ordered Systems, Oct 1987.