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The Optical Activity of the Three-Membered Ring: Oxiranes, Aziridines, Diaziridines, and Oxaziridines

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Abstract: Ab initio SCF–CI methods have been used to study the lower electronic states and the oscillator and optical rotatory strengths of the lower electronic transitions of oxirane, 2-methyloxirane, aziridine, *cis*- and *trans*-2-methylaziridine, diaziridine, 1- and 3-methyldiaziridine, oxaziridine, 2-methyloxaziridine, and *cis*- and *trans*-3-methyloxazirdine. In all species, the lower excited states have considerable diffuseness and are best described as mixed-valence Rydberg states. The first and second electronic transitions of (*S*)-2-methyloxirane are calculated to have negative and positive Cotton effects, respectively, contrary to recent experimental measurements. A rationale for the discrepancy is presented. The calculated and experimental results agree that the first transition of (1*S*,2*S*)-2-methylaziridine has a positive rotational strength. The signs of the CD of all the lower electronic transitions with the possible exception of the second are determined by the configuration at N. The first two transitions of (*R*,*R*)-diaziridine, (*R*,*R*)-1-methyldiaziridine, and (*R*,*R*)-3-methyldiaziridine are both levorotatory. (*R*)-Oxaziridine and (*R*)-2-methyl-(2*R*,3*R*)-3-methyl- and (2*S*,3*R*)-3-methyloxaziridine are calculated to have levorotatory first transitions. The latter results suggest that the optical activity of oxaziridines may not be dominated by the configuration at N.

Introduction

As examples of molecules whose geometric parameters exhibit gross deviations from optimal values, the three-membered ring compounds have been the subjects of considerable interest from experimentalists and theoreticians. Angular constriction and the presence of adjacent heteroatoms greatly increase the magnitude of inversion barriers at tricoordinated atoms.[1] As a consequence, diaziridines and oxaziridines, where both effects are operative, may be configurationally stable at room temperature and numerous examples of resolved chiral diaziridines and oxaziridines may be found in the chemical literature, although the parent compounds have not been resolved. The other stable three-membered ring compounds, oxiranes, aziridines, and cyclopropanes, may be rendered chiral by appropriate derivatization. In fact, the information about the electronic structure and absolute configurations inherent in the circular dichroism (CD) spectra of chiral substances have not been significantly exploited in the case of the three-membered ring compounds. The present theoretical study of the chiroptical properties of the simple three-ring heterocycles is intended to lay a foundation for and to stimulate further experimental and theoretical investigations of these systems.

Theory

A brief description of the theoretical method for the determination of oscillator and optical rotatory strengths is given below. The theory has been presented in detail elsewhere.[2]

Partially correlated wave functions for the ground and excited states of the molecular system are determined to be first order by the Rayleigh–Schrodinger perturbation theory. Thus

$$\psi_n = \psi_n{}^0 - \sum_j \frac{\langle \psi_n{}^0 | \mathcal{H} | \Phi_j{}^0 \rangle}{\langle \Phi_j{}^0 | \mathcal{H} | \Phi_j{}^0 \rangle - \langle \psi_n{}^0 | \mathcal{H} | \psi_n{}^0 \rangle} \Phi_j{}^0 \qquad (1)$$

where $\mathcal{H}$ is the exact electronic Hamiltonian operator, $\Phi_j{}^0$ is a singlet configuration constructed from one or more electron replacements in the Hartree–Fock determinant, Φ_{HF}, and $\psi_n{}^0$ is, in general, a linear combination of quasi-degenerate quasi-degenerate $\varphi_l{}^0$ ($l \neq j$) obtained by diagonalizing a small block of the complete Hamiltonian matrix over the allowed set of configurations. The function $\psi_n{}^0$ is regarded as the "zero-order" part of the wave function and the set $\Phi_j{}^0$ as "first-order" corrections. Considerable economy is realized by the assumption that doubly or more highly excited configurations do not contribute to $\psi_n{}^0$. For the ground state ($\psi_0{}^0 = \Phi_{\mathrm{HF}}$), the first-order corrections are derived from the space of all doubly excited configurations excluding excitations from the core "1s" orbitals. As a result of these approximations, there are no first-order contributions to the values of transition moments (over one-electron operators) which arise from doubly or more highly excited configurations in the excited-state description. Accordingly, only single excitation CI is performed to obtain the excited-state description. Contributions of the doubly excited configurations of the ground-state description, ψ_0, are present in the moments to first order and these are included.

The electric dipole operator, $\vec{\mu}$, the magnetic dipole operator, $\vec{\mathbf{m}}$, and the gradient operator, $\vec{\Delta}$, in atomic units, are given by eq 2–4, where the sums run over all the electrons.

$$\vec{\mu} = \sum_j \vec{\mathbf{r}}_j \qquad (2)$$

$$\vec{\mathbf{m}} = -\sum_j i\left(\vec{\mathbf{r}}_j \times \frac{\partial}{\partial \vec{\mathbf{r}}_j}\right) \qquad (3)$$

$$\vec{\nabla} = \sum_j \frac{\partial}{\partial \vec{\mathbf{r}}_j} \qquad (4)$$

The energy of the excited state, $\Delta E_n{}^{\mathrm{CI}}$ relative to the Hartree–Fock energy, is calculated to second order in perturbation theory within the space of all singly excited configurations. This energy is taken as the calculated excitation energy for the transition. Excitation energies calculated in this way may be too high by as much as 1–2 eV since a description of the reorganization of the "unexcited" electrons which accompanies the excitation process requires the inclusion of doubly and triply excited configurations in the ground- and excited-state wave functions, respectively.

Absence of such configurations leads to an error due to a noncancellation of the neglected correlation energies of the two states and orbital relaxation of the upper state. Fortunately in the present case, where all of the lower excited states have much Rydberg character, the magnitude of the relaxation and correlation error may be estimated empirically if the ionization potential is known. Because the "unexcited" part of the state resembles the molecular positive ion, the Koopmans' defect, the discrepancy between the experimental ionization potential, IP_i, of a particular orbital, i, and the value estimated by Koopmans' theorem, $-\epsilon_i$, can serve as an estimate for this error. Thus a better estimate for excitation to Rydberg states may be obtained by computing

$$\Delta E_n = \Delta E_n{}^{\mathrm{CI}} - (\mathrm{IP}_i + \epsilon_i) \qquad (5)$$

A vertical electronic transition between the ground state ψ_0 and an excited state ψ_n is characterized by the oscillator strength, f_{0n},

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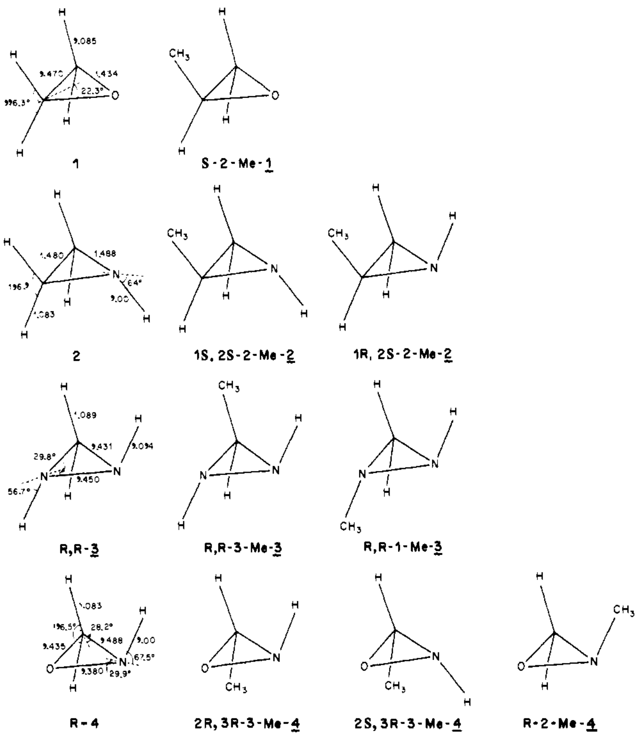

Figure 1. Geometries and absolute configurations of the oxiranes (**1**), aziridines (**2**), diaziridines (**3**), and oxaziridines (**4**).

and optical rotatory strength, $[R_{on}]^r$, which (the latter in atomic units) are given by eq 6 and 7. Instead of $[R_{on}]^r$, one may use

$$f_{on} = \tfrac{2}{3}\langle\psi_0|\vec{\nabla}|\psi_n\rangle\langle\psi_n|\vec{\mu}|\psi_0\rangle \qquad (6)$$

$$[R_{on}]^r = -i\langle\psi_0|\vec{\mu}|\psi_n\rangle\langle\psi_n\rangle\langle\psi_n|\vec{m}|\psi_0\rangle \qquad (7)$$

the origin-independent form[3] of the rotational strength, $[R_{on}]\nabla$, where

$$[R_{on}]^{\nabla} = -i\langle\psi_0|\vec{\nabla}|\psi_n\rangle\langle\psi_n|\vec{m}|\psi_0\rangle/(E_n - E_0) \qquad (8)$$

Agreement between the two forms, (7) and (8), serves as a check on the quality of the wave functions. Both forms are reported in the tables.

Method

All Hartree–Fock SCF calculations were performed by using the GAUSSIAN 70 system of programs.[4a] The internal 6-31G basis set[4b] was augmented in the case of the N and O by the addition of a single diffuse 2s and a set of diffuse 2p functions (exponent 0.028 for N and 0.036 for O).[5] This basis set is adequate to give a good description of the molecular closed-shell ground state and lower valence excited states and should also give a reasonable description of the lowest "3s" and "3p" molecular Rydberg excited states.

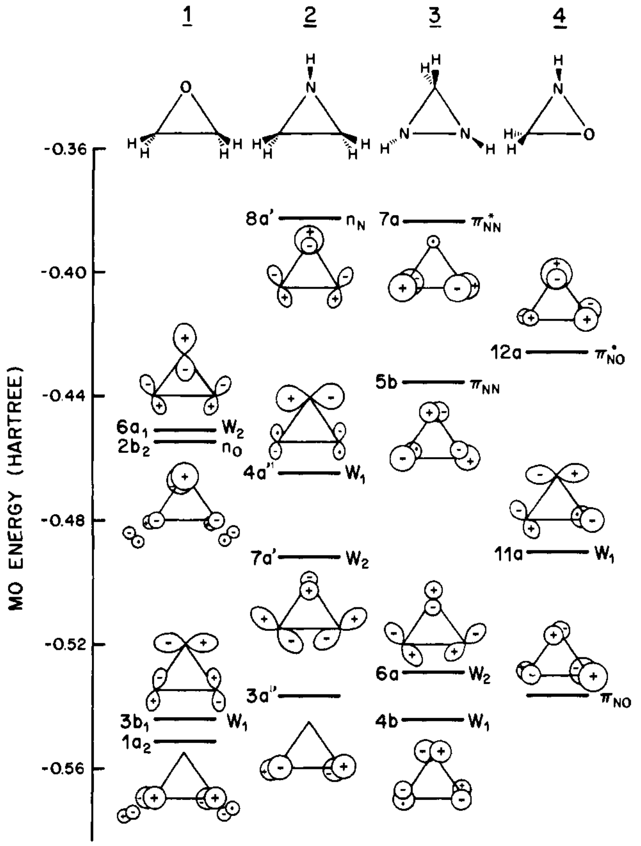

Figure 2. The higher occupied molecular orbitals of the parent compounds as linear combinations of hybridized atomic orbitals. The relative sizes of the AO's are approximately proportional to the magnitudes of the coefficients.

The experimental geometries of oxirane, **1**,[7a] and aziridine, **2**,[7b] were used. The geometry of diaziridine, **3**, was adapted from the X-ray structure of (−)-(1*R*,2*S*)-1-[(*S*)-(1-phenylethyl)carbamoyl]-2-methyl-3,3-pentamethylenediaziridine.[8] For oxaziridine, **4**, the geometry employed in a previous theoretical investigation was used.[9] Geometries of methyl derivatives were generated in each case by replacement of a hydrogen atom by a tetrahedral methyl group (r_{CH} = 1.095 Å) situated at an appropriate distance (r_{NMe} = 1.472 Å, r_{CMe} = 1.513 Å). The details of the geometries and absolute configurations are shown in Figure 1.

Results and Discussion

General Remarks. Although the three-ring heterocycles have been the subject of a number of theoretical investigations (**1**,[10-18]

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(3) A. Moscowitz in "Modern Quantum Chemistry", Vol. 3, O. Sinanoglu, Ed., Academic Press, New York, 1965, p 31.

(4) (a) The GAUSSIAN 70 series of programs (W. J. Hehre, W. A. Lathan, R. Ditchfield, M. D. Newton, and J. A. Pople, Program No. 236, Quantum Chemistry Program Exchange, University of Indiana, Bloomington, Ind.) was modified for this study. (b) W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.*, **56**, 2257–61 (1972).

(5) The diffuse basis set, which had to be limited for practical reasons, is centered on the heteratoms since ionization, or excitation to a Rydberg orbital, of an electron from the nonbonded molecular orbitals leaves a positive hole highly localized to the heteroatom. Orbital relaxation may delocalize or move the hole but its description requires interaction of doubly and triply excited (relative to Φ_{SCF}) configurations which are not included in the present CI procedure. Experience with the calculation of ionization potentials has demonstrated that the Koopmans' defect is more important for localized holes.[6]

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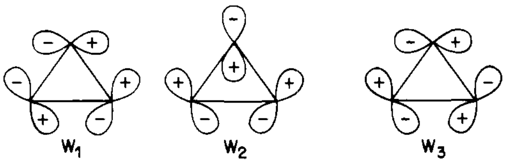
Table I. Results for Oxirane (1) and (S)-2-Methyloxirane ((*S*)-2-Me-1)

		1	exptl	(*S*)-2-Me-1	exptl
E_{SCF}, hartree		−152.785 55		−191.812 07	
HOMO		W_2 $6a_1$ −12.27[a]	11.71[b]	W_2 16a −11.78	11.23[b]
MO energies, eV		n_0 $2b_2$ −12.37[a]	10.57	n_0 15a −12.17	10.26
		$3b_1$ −14.80	13.7	14a −14.05	12.88
		$1a_2$ −15.00	14.2	13a −14.38	13.33
μ, D		2.96	1.88[c]	2.96	
$S_0 \to S_1$	ΔE, eV	9.27 (7.47)[d]	7.24	9.40 (7.49)[d]	7.13[f]
	$[R]$[e]			−4.4 (−3.9)[e]	(+)
	f	0.0079		0.0113	
	description	$A_1 \to B_2$, $2b_2 \to na_1$, $n_0 \to 3s_0$, σ^*_{CO}		72% ($n_0 \to \sigma^*_{\text{CO}}$, $3s_0$)	
$S_0 \to S_2$	ΔE, eV	9.73 (9.17)[d]		9.67 (9.12)[d]	
	$[R]$			16.7 (16.9)	
	f	0.0475		0.0212	
	description	$A_1 \to A_1$, $6a_1 \to na_1$, $W_2 \to 3s_0$		74% ($W_2 \to 3s_0$)	
$S_0 \to S_3$	ΔE, eV	9.85 (8.05)	7.8	9.82 (9.27)	
	$[R]$			−4.4 (−6.9)	
	f	0.0000		0.0417	
	description	$A_1 \to A_2$, $2b_2 \to nb_1$, $n_0 \to W_3$		$W_2 \to 3p$	
$S_0 \to S_4$	ΔE, eV	9.97 (9.41)		10.07 (9.52)	
	$[R]$			−4.0 (−4.5)	
	f	0.0510		0.0360	
	description	$A_1 \to A_1$, $6a_1 \to na_1$, $W_2 \to 3p_0$		72% ($W_2 \to 3p$)	
$S_0 \to S_5$	ΔE, eV	10.02 (8.22)	7.89	10.10 (8.19)	
	$[R]$			13.3 (6.3)	
	f	0.0381		0.0148	
	description	$A_1 \to B_2$, $2b_2 \to na_1$, $n_0 \to 3p$		71% ($n_0 \to 3p$)	
$S_0 \to S_6$	ΔE, eV	10.28 (9.72)		10.30 (8.39)	
	$[R]$			−1.4 (−0.00)	
	f	0.0652		0.0182	
	description	$A_1 \to B_1$, $6a_1 \to nb_1$, $W_2 \to 3p$		$n_0 \to \sigma^*$	
$S_0 \to S_7$	ΔE, eV	10.38 (8.58)	8.18	10.46 (9.91)	
	$[R]$			21.4 (17.4)	
	f	0.0234		0.0086	
	description	$A_1 \to A_1$, $2b_2 \to nb_2$, $n_0 \to 3p$		$W_2 \to \sigma^*_{\text{C-H}}$ (methyl)	

[a] The order of these orbitals is basis set dependent (see ref 12, 18). [b] Reference 12. [c] Reference 28. [d] Values in parentheses are excitation energies after use of eq 5. [e] Rotational strength given as $[R]^r$ ($[R]^\nabla$) in cgs × 10^{-40}.

2,[9,15-21] **3**,[18,22] **4**[9,22-26]), relatively few studies have attempted to assign the electronic spectra of these species[11,15,16,18,21,26] and there are only two reports of theoretical investigations into the optical activity of the systems under consideration here.[14,21]

Before species **1**–**4** are discussed individually, some general observations may help to reveal a pattern in the computed results. The higher occupied orbitals of the parent compounds are shown in Figure 2. The MO's are sketched as linear combinations of hybridized AO's whose relative magnitudes are depicted as roughly proportional to their computed coefficients. The orbitals are identified with the Walsh orbitals of cyclopropane or with nonbonded electron pairs of the heteroatoms (n in the case of **1** and **2**; π^* and π in the case of **3** and **4**). Virtual orbitals are not shown in Figure 2 since, because of configurational mixing, the terminal orbitals of electronic excitations bear little resemblance to the virtual orbitals produced by the SCF procedure. The lowest excited states of all species arise from excitations from the highest occupied molecular orbital (HOMO). The only exception is the oxirane system **1** where n_O and W_2 (Figure 2) are calculated to be nearly degenerate,[18] a finding not at all in accord with experimental ionization potentials[12,18] which show that ionization from W_2 is 1.14 eV more difficult than from n_O. The second and fourth singlet excitations of **1** and the second, third, and fourth of 2-Me-**1** are calculated to arise from W_2. The Koopmans' defect[6b] is larger than in any of the other systems. The results of correction by eq 5 in systems **1**–**3** are shown in Tables I–IV.



The upper orbital of all of the excited states of all of the compounds in this investigation is quite diffuse. Whether the states should be regarded as being a "Rydberg state" or as having "mixed-valence Rydberg" character is a moot point. In the tables, the states are described as much as possible in valence or Rydberg terminology and the upper orbitals are described as "3s", "3p", "W_3", or "σ^*" wherever such descriptions seem appropriate. Such an analysis is possible by taking advantage of the following property of determinantal wave functions

$$\sum_k c_k \Phi(\phi_i \to \phi_k) = \Phi(\phi_i \to \sum_k c_k \phi_k) \qquad (9)$$

where ϕ_k is an SCF virtual orbital.

Oxiranes. 1 and (*S*)-2-Me-1. The results for **1** and (*S*)-2-Me-**1** are shown in Table I. As pointed out above, the oxirane system is anomalous computationally in that Koopmans' theorem leads to a very poor estimate of the ionization potentials from the HOMO (W_2) and highest subjacent MO (n_O).[18] The discrepancy persists in the methyl derivative as can be seen by comparing the experimental ionization potentials.[12] The Koopmans' defects of the two highest orbitals of **1** and 2-Me-**1** give an indication that the neglected more highly excited configurations will play a greater

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Table II. Results for Aziridine (**2**) and (1*S*,2*S*)- and (1*R*,2*S*)-2-Methylaziridine

	2	exptl	(1*S*,2*S*)-2-Me-**2**	exptl	(1*R*,2*S*)-2-Me-**2**
E_{SCF}, hartree	−132.963 81		−171.988 56		−171.986 81
HOMO	n_N $8a^1$ −10.40	9.88[a]	n_N 16a −10.27		n_N 16a −10.16
MO energies, eV	W_1 $4a^{11}$ −12.62	11.8	W_1 15a −12.18		W_1 15a −12.26
	$7a^1$ −13.37		14a −12.75		14a −12.90
	$3a^{11}$ −14.61		13a −13.97		13a −14.08
μ, D	2.44	1.89[b]	2.34		2.50
$S_0 \rightarrow S_1$ ΔE, eV	7.12 (6.60)[c]	6.20	7.12	6.20[d]	7.26
[*R*]			6.0 (6.5)[f]	(+)[d]	−4.7 (−11.4)[f]
f	0.0116		0.0080		0.0299
description	$A^1 \rightarrow A^1$, $8a^1 \rightarrow na^1$, $n_N \rightarrow$ 3s		$n_N \rightarrow$ 3s3p		$n_N \rightarrow$ 3s3p
$S_0 \rightarrow S_2$ ΔE, eV	8.17 (7.65)		8.11		7.99
[*R*]			−7.6 (−7.8)		−2.9 (1.7)
f	0.0000		0.0445		0.0300
description	$A^1 \rightarrow A^{11}$, $8a^1 \rightarrow na^{11}$, $n_N \rightarrow$ 3p		$n_N \rightarrow$ 3p		$n_N \rightarrow$ 3p
$S_0 \rightarrow S_3$ ΔE, eV	8.17 (7.65)	7.19[a]	8.25		8.17
[*R*]			−3.9 (−0.4)		6.4 (2.4)
f	0.0770	0.086[e]	0.0483		0.0051
description	$A^1 \rightarrow A^1$, $8a^1 \rightarrow na^1$, $n_N \rightarrow$ 3p		$n_N \rightarrow$ 3p		$n_N \rightarrow$ 3p
$S_0 \rightarrow S_4$ ΔE, eV	8.28 (7.76)		8.67		8.40
[*R*]			15.4 (9.9)		−10.3 (−11.4)
f	0.0184		0.0170		0.0187
description	$A^1 \rightarrow A^1$, $8a^1 \rightarrow na^1$, $n_N \rightarrow$ 3p		$n_N \rightarrow$ 3p		$n_N \rightarrow$ 3p
$S_0 \rightarrow S_5$ ΔE, eV	9.45 (8.60)		9.2		9.53
[*R*]			6.1 (6.7)		−6.6 (−3.3)
f	0.0004		0.0051		0.0131
description	$A^1 \rightarrow A^{11}$, $4a^{11} \rightarrow na^1$, $W_1 \rightarrow$ 3s3p		$W_1 \rightarrow$ 3s3p		$W_1 \rightarrow$ 3s3p

[a] Reference 18. [b] Reference 32. [c] Values in parentheses are excitation energies after use of eq 5. [d] Reference 21, experimental value. [e] Reference 27. [f] Rotational strengths are given as $[R]^r$ ($[R]^\nabla$) in cgs × 10^{-40}.

Table III. Results for (*R*, *R*)-Diaziridine ((*R*, *R*)-**3**) and (*R*, *R*)-3- and (*R*, *R*)-1-Methyldiaziridine

	(*R*, *R*)-**3**	(*R*, *R*)-3-Me-**3**	(*R*, *R*)-1-Me-**3**
E_{SCF}, hartree	−148.903 98	−187.931 54	−187.919 85
HOMO	π^*_N 7a −10.43 (10.4)[a]	π^*_N 16a −10.32 (9.90)[b]	π^*_N 16a −10.09 (9.20)[c]
MO energies, eV	π^*_N 5b −11.84	π^*_N 15a −11.53	π^*_N 15a −11.43
	W_2 6a −14.40	14a −13.79	14a −13.37
	W_1 4b −14.81	13a −13.89	13a −14.22
μ, D	1.67	1.87	1.44
$S_0 \rightarrow S_1$ ΔE, eV	7.03	7.10 (6.68)[d]	7.90 (6.20)[d]
[*R*]	−13.2 (−14.0)[e]	−12.9 (−11.5)[e]	−14.2 (−12.9)[e]
f	0.0419	0.0375	0.0112
description	A → B, 7a → *n*b, $\pi^*_N \rightarrow \sigma^*_{NN}$, 3p	$\pi^*_N \rightarrow \sigma^*_{NN}$, 3p	$\pi^*_N \rightarrow \sigma^*_{NN}$, 3p
$S_0 \rightarrow S_2$ ΔE, eV	7.27	7.32 (6.90)	7.67 (6.78)
[*R*]	−19.8 (−16.2)	−14.5 (−10.9)	−4.0 (−3.8)
f	0.0025	0.0119	0.0476
description	A → A, 7a → *n*a, $\pi^*_N \rightarrow$ 3s	$\pi^*_N \rightarrow$ 3s	$\pi^*_N \rightarrow$ 3p
$S_0 \rightarrow S_3$ ΔE, eV	8.09	8.05 (7.63)	8.01 (7.12)
[*R*]	16.0 (24.3)	16.5 (22.5)	0.3 (3.8)
f	0.0768	0.0662	0.0107
description	A → B, 7a → *n*b, $\pi^*_N \rightarrow$ 3p	$\pi^*_N \rightarrow$ 3p	$\pi^*_N \rightarrow$ 3p
$S_0 \rightarrow S_4$ ΔE, eV	8.18	8.37 (7.95)	8.26 (7.37)
[*R*]	−0.8 (−0.7)	0.4 (3.2)	35.8 (27.1)
f	0.0041	0.0117	0.0483
description	A → A, 7a → *n*a, $\pi^*_N \rightarrow$ 3p	$\pi^*_N \rightarrow$ 3p	$\pi^*_N \rightarrow$ 3s
$S_0 \rightarrow S_5$ ΔE, eV	8.73	8.65	8.53
[*R*]	0.9 (3.0)	−9.4 (−7.4)	−10.4 (−6.9)
f	0.0002	0.0015	0.0035
description	A → A, 5b → *n*b, $\pi_N \rightarrow \sigma^*_{NN}$, 3p	83% ($\pi_N \rightarrow \sigma^*_{NN}$, 3p)	62% ($\pi_N \rightarrow \sigma^*_{NN}$, 3s)

[a] Estimated in ref 34. [b] IP of 3,3-dimethyl-**3**.[34] [c] IP of 1,3,3-trimethyl-**3**.[34] [d] Values in parentheses are excitation energies after use of eq 5. [e] Rotational strengths are given as $[R]^r$($[R]\Delta$) in cgs × 10^{-40}.

role in the description of electronic states originating via n_O excitations than those that arise via W_2 excitations. Application of eq 5 to **1** and 2-Me-**1** changes the order of some of the lower excited states. In the case of **1**, each of the singlet states can be described as arising more than 95% via excitation from a single orbital, n_O or W_2. This is not true in the case of 2-Me-**1** where there is a greater mixture of the two types of excitation in each state as shown in Table I. In the latter case, eq 5 has been applied for the major component to give a better indication of the proper ordering of states. It is entirely possible that the extent of admixture of the different originating orbitals is exaggerated because of the near degeneracy of n_O and W_2 and the omission of more

Table IV. Results for (R)-Oxaziridine ((R)-4)) and ($2R$,$3R$)-3-Methyl-, ($2S$,$3R$)-3-Methyl-, and (R)-2-Methyloxaziridine

	(R)-4	($2R$,$3R$)-3-Me-4	($2S$,$3R$)-3-Me-4	(R)-2-Me-4
E_{SCF}, (hartree)	−168.699 96	−207.730 96	−207.729 24	−207.714 27
HOMO	π^*_{NO} 12a −11.58	π^*_{NO} 16a −11.36	π^*_{NO} 16a −11.25	π^*_{NO} 16a −11.13
MO energies, eV	W_2 11a −13.34	15a −12.73	15a −12.86	15a −12.77
	π_{NO} 10a −14.59	14a −13.95	14a −14.08	14a −13.90
	W_1 9a −16.46	13a −14.84	13a −15.23	13a −15.35
μ, D	3.54	3.50	3.88	3.47
$S_0 \rightarrow S_1$ ΔE, eV	7.74	7.73	7.80	8.03
[R]	−11.1 (−13.4)[a]	−6.3 (−6.1)	−2.6 (−4.7)	−23.6 (−18.2)
f	0.0283	0.0219	0.0300	0.0250
description	$\pi^*_{NO} \rightarrow \sigma^*_{NO}$, $3s_N$	$\pi^*_{NO} \rightarrow 3s_N$, σ^*_{NO}	$\pi^*_{NO} \rightarrow \sigma^*_{NO}$, $3s_N$	$\pi^*_{NO} \rightarrow 3s_N$
$S_0 \rightarrow S_2$ ΔE, eV	8.29	8.33	8.31	8.53
[R]	−2.2 (−5.5)	−2.2 (−3.8)	9.2 (8.2)	−7.74 (−4.02)
f	0.0105	0.0061	0.0062	0.0030
description	$\pi^*_{NO} \rightarrow \sigma^*_{NO}$	$\pi^*_{NO} \rightarrow W_3$	$\pi^*_{NO} \rightarrow 3p$	$\pi^*_{NO} \rightarrow W_3$
$S_0 \rightarrow S_3$ ΔE, eV	8.28	8.87	8.69	8.54
[R]	3.2 (13.0)	−19.0 (−14.2)	−1.1 (−12.2)	4.7 (7.1)
f	0.0195	0.0468	0.0484	0.0033
description	($\pi^*_{NO} \rightarrow W_3$), 8% (11a $\rightarrow W_3$)	$\pi^*_{NO} \rightarrow 3p$	91% ($\pi^*_{NO} \rightarrow W_3$)	$\pi^*_{NO} \rightarrow 3p$
$S_0 \rightarrow S_4$ ΔE, eV	9.08	9.03	8.94	8.88
[R]	4.4 (5.9)	17.4 (19.2)	1.6 (2.1)	16.8 (17.7)
f	0.0069	0.0148	0.0094	0.0537
description	$\pi^*_{NO} \rightarrow 3p$	$\pi^*_{NO} \rightarrow 3p$	$\pi^*_{NO} \rightarrow 3p$	$\pi^*_{NO} \rightarrow 3p$
$S_0 \rightarrow S_5$ ΔE, eV	9.30	9.32	9.31	9.20
[R]	−6.4 (−7.0)	−9.2 (−4.6)	−5.6 (−4.0)	7.7 (1.3)
f	0.0483	0.0180	0.0167	0.0165
description	$\pi^*_{NO} \rightarrow 3p$	$\pi^*_{NO} \rightarrow 3p$	$\pi^*_{NO} \rightarrow 3p$	$\pi^*_{NO} \rightarrow 3p$

[a] Rotational strengths are given as $[R]^r$ ($[R]^\nabla$) in cgs × 10^{-40}.

highly excited configurations and that this fact will be reflected in the calculated one-electron transition properties. The most serious consequence occurs in the calculated rotational strengths if the electric and magnetic dipole transition moments are nearly perpendicular. In this case, small changes in the direction of the moments may lead to a reversal of the sign of the [R]. Such changes may be due to artifacts arising from computational deficiencies, or they may be caused by external perturbations such as solvation. With the above *caveat* in mind, the correspondence between experimental observations and computed results is discussed below.

Application of eq 5 yields the result that the ordering of excited states of **1** is B_2 (7.41 eV) < A_2 (8.05 eV) < B_2 (8.22 eV) < A_1 (8.58 eV) < A_1 (9.16 eV) < A_1 (9.40 eV). Sharp features in the experimental gas-phase spectrum of **1** have been assigned to Rydberg transitions $n_O \rightarrow 3s$ (7.24 eV), $n_O \rightarrow 3p$ (7.89 eV), $n_O \rightarrow 4s$ (8.64 eV), and $n_O \rightarrow 3d$ (8.96 eV).[27] In a polycrystalline film, the sharp features are replaced by a broad absorption with maxima of 8.68 and 10.5 eV and a barely discernible shoulder of 7.8 eV.[27] The first state is described in Table I as n $\rightarrow$ ($3s_O$,σ_{CO}^*), indicating that while the principal component of the terminal MO is an orbital mainly situated on oxygen and with the nodal characteristics of an atomic "3s" orbital, there is also a substantial antibonding component from the s orbitals on the C atoms. The second state of A_2 symmetry is assigned to the weak shoulder at 7.8 eV in the polycrystalline film. The terminal orbital of the transition resembles W_3 with an admixture of $3p_O$ and, though quite diffuse ($\langle r^2 \rangle$ = 17.6 bohr^2), is the most compact of all of the upper orbitals of the present study. The third state is satisfactorily described as $n_O \rightarrow 3p$ Rydberg and is associated with the sharp features at 7.89 eV in agreement with previous assignments. The calculations indicate the presence of a second $n_O \rightarrow 3p$ transition ($S_0 \rightarrow S_7$, $A_1 \rightarrow A_1$, $2b_2 \rightarrow nb_2$) separated from the first by 0.36 eV and having oscillator strength f = 0.0234. There is no band at the position predicted by the separation from the 7.89-eV band in the spectrum. It is possible that this transition coincides with what has previously been assumed to be the third vibrational component of the 7.89-eV band which occurs at 8.18 eV. In Table I, this association has been made. The only alternative is the 8.64-eV band which has been identified with the $n_O \rightarrow 4s$ transition and which is not describable with the present basis set.

The three transitions from W_2, namely, $S_0 \rightarrow S_2$, $S_0 \rightarrow S_4$, and $S_0 \rightarrow S_6$ in Table I, are calculated to have a combined oscillator strength of 0.1637 and an average energy of 9.43 eV. These values compare reasonably with the solid-state experimental values if it is assumed that there are three transitions under the broad absorption from 8 to 9.5 eV with a maximum at 8.68 and a total oscillator strength of about 0.15. Basch et al. have assigned this band to a $6a_1 \rightarrow \sigma^*$ ($^1A_1 \rightarrow {}^1A_1$) valence transition.[18] Although the $S_0 \rightarrow S_4$ transition is $^1A_1 \rightarrow {}^1A_1$ ($6a_1 \rightarrow na_1$) and the calculated oscillator strength is the second largest of the low-lying transitions, the terminal orbital is labeled as $3p_O$ instead of σ^* on the basis of its diffuseness ($\langle r^2 \rangle$ = 37.8 bohr^2). The transition $W_2 \rightarrow 3p$ ($S_0 \rightarrow S_6$) terminates in a 3p orbital perpendicular to the ring.

The most valence-like transition with a large oscillator strength is calculated to be $S_0 \rightarrow S_{12}$, ΔE = 12.21 eV (10.41 eV by using eq 5), f = 0.3097. On the basis of the calculated intensity, this transition must be responsible for the broad band peaking at 10.5 eV in the spectrum of condensed **1**.

Pure (S)-2-Me-**1** has $[\alpha]^{20}_D = -14.65 \pm 0.05$ (neat).[29] Both $[\alpha]_D$[30a] and the ORD[30b] spectrum are solvent dependent, the latter changing sign at 4.1 eV for the neat sample as well as in chloroform solution, but not in benzene. The first transition of (S)-2-Me-**1** is calculated to be at 7.49 eV (by using eq 5) and to have a small negative rotational strength. By analysis using eq 9 the composition of the excited state may be described as 72% (1Sa $\rightarrow$ na, $n_O \rightarrow 3s$, σ^*_{CO}), 27% (1ba $\rightarrow$ na, $W_2 \rightarrow 3p_O$). The "3p" of the weaker component is perpendicular to the ring and extensively delocalized over the entire molecule. The transition has a strong magnetic dipole transition moment (0.54 au) ap-

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proximately parallel to the C_2C_3 bond and a weaker electric dipole transition moment (0.22 au) in the plane of the bisector of the ring, tilted from the plane of the ring on the methyl side by 29°. The two moments are nearly perpendicular, thus accounting for the weak rotatory strength. As pointed out above, under these circumstances, the sign of the rotatory strength may be uncertain computationally or it may be subject to change due to external perturbations which may shift the directions of the transition moments. Indeed, after the present calculations were completed, we received a communication of the results of experimental CD measurements on (*S*)-2-Me-**1**. Although the work is not complete, it appears that the first transition of (*S*)-2-Me-**1** has a very weak CD as expected, but *positive* in sign, contrary to the results obtained by the present method.[31] Experimental CD measurements of (−)-(*S*,*S*)-2,3-dimethyloxirane reveal a strong positive CD bond for the $n_O \rightarrow 3s$ transition.[31] The optical rotation of 2-Me-**1** has been studied theoretically by computation from single atom polarizabilities.[14] Although variation of the magnitude as a function of methyl rotation was found, no change of sign was predicted. In any case, among the lower energy excited states which should be reasonably well described within the limitations of the basis set and CI formulation used in the present study, there is no indication of a dominant levorotatory transition for the *S* epimer. It is hoped that the results cited above and included in Table I may encourage further theoretical investigation of this system.

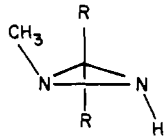
Aziridines. 2, (1*S*,2*S*)-2-Me-2, and (1*R*,2*S*)-2-Me-2. The results for **2**, (1*S*,2*S*)-2-Me-**2**, and (1*R*,2*S*)-2-Me-**2** are shown in Table II. The higher occupied MO's of **2** are shown in Figure 2. The HOMO, which is highly localized to N and corresponds to the N lone pair, n_N, is energetically well separated from the next highest occupied MO, W_1. In this system, as in **3** and **4**, there should be none of the computational difficulties experienced with **1**. Assignments of the aziridine spectrum have been discussed at length by Robin.[27] The calculated results are in complete accord with the earlier assignments. All of the lower states are calculated to be Rydberg-like ($\langle r^2 \rangle$ in the range 30–50 bohr^2). The most intense transition $S_0 \rightarrow S_3$ is polarized parallel to the mirror plane and tilted out of the plane of the ring toward the lone pair by 22°.

(2*S*)-2-Methylaziridine exists as an equilibrium mixture of the 1*S*,2*S* and 1*R*,2*S* diasteriomeric forms in 4:1 ratio at room temperature[33] and is levorotatory. The isomeric species have been investigated experimentally and theoretically by Gottarelli et al.[21] The experimental UV spectrum of (2*S*)-2-Me-**2** reveals only a shoulder at about 6.20 eV in solution, but, in the gas-phase spectrum, several sharp transitions which are components of a Rydberg transition beginning at 6.33 eV are observed.[21] The first band has a positive circular dichroism, the negative sign of optical rotation at the sodium D lines evidently being due to transitions in the inaccessible part of the UV.

The present results are qualitatively similar to those of Gottarelli and co-workers, who employed a somewhat more limited basis set and a different CI procedure.[21] Both studies concur that the first transition is a Rydberg transition with a positive rotational strength, in agreement with experiment. Our results differ in that the calculated rotatory strength of the second transition of (1*S*,2*S*)-2-Me-**2** has a larger negative value than theirs. However, the sign of the second transition of the cis isomer is indeterminate, the computed value of $[R]^r$ disagreeing in sign with that of $[R]^\nabla$. With the possible exception of the second transition, the rotational strengths of all of the lower transitions change sign with inversion of configuration at N.

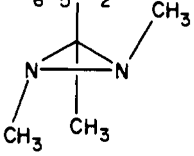
Diaziridines. (*R*,*R*)-3, (*R*,*R*)-3-Me-3, and (*R*,*R*)-1-Me-3. The computed results for the diaziridines are shown in Table III, and the orbitals of **3** are portrayed in Figure 2. The two highest occupied MO's are the π and π^* combinations of the nonbonded electrons of N, labeled π_N and π^*_N, respectively. The four lowest excitations of **3** as well as of the methyl derivatives originate from π^*_N and terminate in Rydberg orbitals ($\langle r^2 \rangle$ is in the range 30–50 bohr^2). The first transition in each case terminates in an orbital identified as 3p, directed along the N–N bond and having substantial antibonding contributions from the s orbitals of N. Substitution of a methyl on the C atom has little effect on the computed properties, $[R]$ or f, of the transitions originating from π^*_N but leads to an increased rotatory strength for the transition originating from π_N. Methyl substitution at N has a more profound effect as might be expected from the resulting reduction of the local symmetry. However, the description and rotatory strength of the first transition are similar to those of the other two diaziridines, the oscillator strength having been reduced by a factor of 3. The next three transitions have undergone considerable shuffling as a result of N-methylation, and the descriptions of the diffuse terminal orbitals as "3s" and "3p" must not be taken literally. The fourth transition has the largest rotatory strength calculated for the present series.

A number of optically active substituted diaziridines have been prepared and characterized, mainly by Kostyanovskii and co-workers[8,35–38] and by Mannschreck and co-workers.[39] Diaziridines **5a–c**, in which the only source of chirality is due to N, are levorotatory with the absolute configurations (1*S*,2*S*) shown.[8,36–38] Kostyanovskii has shown that racemization proceeds by inversion at the nitrogen atoms rather than by an exchange of groups.[35] The analogous compound in the present study is (*R*,*R*)-1-Me-**3** for which the first transition (at 6.2 eV) has a substantial negative rotatory strength. This result is in excellent agreement with experimental results since both **5b** and **5c** with the (*S*,*S*) absolute configuration have positive $\Delta\epsilon_{max}$ for the lowest energy transition (at 6.29 eV for **5b** and 6.11 eV for **5c**). The observed sign of optical rotation at the sodium D lines of the 1-methyl derivatives opposite to that of the lowest energy transition may be attributed to the fourth transition estimated to occur at 7.37 eV (168 nm).



5a, R = CO_2Me
5b, R, R = $-CH_2(CH_2)_3CH_2-$
5c, R = CH_3

It is of interest that the levorotatory form of the symmetrically substituted diaziridine **6** ($[\alpha]^{22}_{436}$ = −141° (CCl_4)) has a region of weak negative CD in the region of the aromatic ring absorptions ($\Delta\epsilon$ (268) = −0.12, $\Delta\epsilon$ (262) = −0.12, $\Delta\epsilon$ (256) = −0.08) followed by two maxima with stronger positive CD ($\Delta\epsilon$ (219 nm, 5.66 eV) ≃ +1.6, $\Delta\epsilon$ (214 nm, 5.79 eV) ≃ +1.7) in the region of the diaziridine ring absorptions.[39] One can approximate the effect of methyl substitution of each N on the excitation energies by noting that the ionization potential of 1,2,3,3-tetramethyl-



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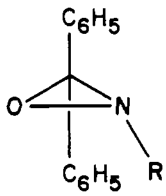
diaziridine is lower by 0.96 eV than that of 3,3-dimethyldiaziridine.[34] By subtracting this amount from the estimated excitation energies for (*R*,*R*)-3-Me-3 (Table I), we can obtain approximate excitation energies for the first two (Rydberg) transitions of the tetraalkyldiaziridine, 5.72 and 5.94 eV, in good agreement with the experimental results for **6**.[39] The calculated negative signs for these two transitions of the (*R*,*R*) compounds, (*R*,*R*)-**3** and (*R*,*R*)-3-Me-**3**, suggests that the absolute configuration of (+)-**6** is also (*R*,*R*).

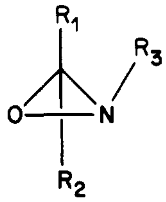
Oxaziridines. (*R*)-4, (2*R*,3*R*)-3-Me-4, (2*S*,3*R*)-3-Me-4, and (*R*)-2-Me-4. The results for the oxaziridines (**4**) are presented in Table IV and the MO's of **4** are shown in Figure 2. The HOMO of **4** is derived from the π^* combination of the nonbonded electrons of N and O and is labeled π^*_{NO} It is well separated from the highest subjacent MO's, a W_1-like orbital and one composed principally of the π combination of the N and O lone pairs. All of the lowest transitions of all of the oxaziridines investigated originate from the HOMO, π^*_{NO}. The terminal orbitals vary in diffuseness. In the case of $S_0 \rightarrow S_1$, $S_0 \rightarrow S_2$, and $S_0 \rightarrow S_3$, $\langle r^2 \rangle$ is 27.7, 23.0, and 22.2 bohr^2, respectively, indicating some valence character for the orbital, whereas for the transitions $S_0 \rightarrow S_4$ and $S_0 \rightarrow S_5$, $\langle r^2 \rangle$ is 49.0 and 44.9 bohr^2, more characteristic of Rydberg transitions.

Optically active oxaziridines have been synthesized for over a decade[40-47] since the first reported synthesis by Montanari and co-workers in 1968.[41] The absolute configuration at chiral N was first established by Bucciarelli et al.[44] in 1976 by X-ray analysis of (−)-(2*S*)-2-[(*R*)-1-phenylethyl]-3,3-diphenyloxaziridine (**7a**).

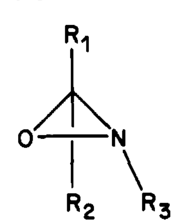


7a, R = (*R*)-1-phenylethyl
7b, R = (*S*)-1-phenylethyl
7c, R = isopropyl
7d, R = *tert*-butyl

This report was followed closely by another[48] establishing the absolute configuration of (+)-(2*R*,3*R*)-2-[(*S*)-1-phenylethyl]-3-(*p*-bromophenyl)oxaziridine (**8a**). The absolute configurations of the remaining diastereoisomers of **8a**, namely, **8b**, **9a** and **9b**, have been established,[49] the cis isomers by the isomerization



8a, R_1 = H, R_2 = *p*-bromophenyl, R_3 = (*S*)-1-phenylethyl
8b, R_1 = *p*-bromophenyl, R_2 = H, R_3 = (*S*)-1-phenylethyl

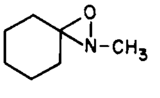


9a, R_1 = H, R_2 = *p*-bromophenyl, R_3 = (*S*)-1-phenylethyl
9b, R_1 = *p*-bromophenyl, R_2 = H, R_3 = (*S*)-1-phenylethyl

conversions **9a** → **8a** and **8b** → **9b**, which were shown to proceed by inversion at N.[50] The absolute configurations of two other oxaziridines have been established by X-ray diffraction, namely, that of **7b**[51] and its epimer.[52] The absolute configurations of numerous other oxaziridines have been related to the above by comparison of ORD and CD data[51,53] and by NMR techniques.[47,54] The levorotatory form is associated with the (*S*) absolute configuration at N independent of the presence of other chiral centers or chromophoric groups in the molecule. The single exception to this "rule of thumb" is **8b** which has the *R* absolute configuration at N but is levorotatory.[49]

The results of our calculations suggest that, as in the case of aziridines **2** and diaziridines **3**, the observed sign of optical rotation at long wavelengths is opposite to the sign of the Cotton effect of the lowest energy transition of the three-membered ring. The parent compound **4** with the *R* absolute configuration at N has a negative CD for its first transition ($\Delta\epsilon$ (calcd) = 7.74 eV, f = 0.0283) which is best described as a mixed-valence Rydberg $\pi^*_{NO} \rightarrow (\sigma^*_{NO}, 3s_N)$ transition. The assessment of the nature of the state is in accord with more rigorous CI calculations on the same system.[26] The negative rotatory strength of the $S_0 \rightarrow S_1$ transition is enhanced by N-alkylation (Table IV). Thus (*R*)-2-Me-**4** has $[R_{S_0S_1}]' = -23.6 \times 10^{-40}$ cgs compared to **4** with $[R_{S_0S_1}] = -11.1 \times 10^{-40}$ cgs. The second and third transitions of **4** are quasi-degenerate with weak oppositely signed CD. The near degeneracy is not lifted by N-alkylation.

Experimentally, 2,3,3-trialkyloxaziridines exhibit weak absorption maxima at about 205 nm: **10**, ϵ_{max} = 112.8 at 207 nm (5.99 eV); **11**, ϵ_{max} = 172 at 200 nm (6.20 eV).[55] Similarly



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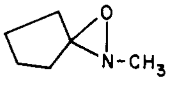

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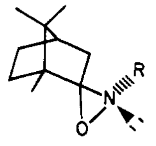

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optically active N-alklyl- and *N*-benzyloxaziridines of the type **12** derived by oxidation of (−)-camphorimines have weak inflection points at about 210 nm (5.90 eV) in their absorption spectra.[53] The levorotatory oxaziridines **12** (R = Me, Et, *i*-Pr, *t*-Bu, $-CH_2C_6H_5$) have been argued to have the *S*,*S* configurations at the asymmetric carbon and nitrogen atoms on the basis of NMR spectroscopy, space-filling molecular models, and the analogy to the stereochemical course observed for other reactions of the bicyclic ring system. The CD of *all* compounds (−)-**12** (R = Me, Et, *i*-Pr, *t*-Bu, $-CH_2C_6H_5$) show a positive Cotton effect in the 210-nm region.[53] Thus the present results support the *S* assignment for the configuration at N and the 210-nm transition cor-

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responds to $S_0 \rightarrow S_1$ ($\pi^*_{NO} \rightarrow (\sigma^*_{NO}, 3s_N)$) of Table IV.

The 3-alkyl derivatives of **4** differ from the parent **4** and its *N*-alkyl derivative 2-Me-**4** in that the quasi-degeneracy of the $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_3$ transitions is lifted. The first three transitions of (2*R*,3*R*)-3-Me-**4** are all calculated to have negative rotatory strengths, the third transition, $\pi^*_{NO} \rightarrow 3p$, displaying appreciable intensity. The cis isomer (2*S*,3*R*)-3-Me-**4** is the only oxaziridine investigated which has the *S* absolute configuration at N and whose first transition has a negative CD. The intensity is weak, however. The CD of the second transition is positive and is of greater magnitude. In none of the species with the *R* configuration at N is there a transition calculated to occur below 10 eV which appears to have a strong enough positive rotatory strength to outweigh the negative CD of the lower transitions.

Conclusions

The lower transitions of all of the oxiranes, aziridines, diaziridines, and oxaziridines of this study originate from nonbonded electron pairs and terminate in diffuse orbitals which have appreciable mixed-valence Rydberg character. A disagreement exists between the calculated and measured sign of the CD of the first transition of (−)-(*S*)-2-Me-**1**. The discrepancy is probably due to the level of CI used in this study which is not able to describe substantial reorganization of the "unexcited" electrons. In the oxirane system, the only one of the present systems where such reorganization is important as suggested by the magnitude of the Koopmans' defect, the consequent inadequate description of the lower excited states apparently results in the wrong computed sign of the CD of the first (and possibly other) transitions.

The first transition of (−)-(1*S*,2*S*)-2-methylaziridine has a positive rotational strength. The signs of the CD of all of the lower electronic transitions of this compound with the possible exception of the second are determined by the configuration at N rather than at C.

The first two transitions of (*R*,*R*)-diaziridine and (*R*,*R*)-1-methyl- and (*R*,*R*)-3-methyldiaziridine both have negative CD. In the chiral diaziridines where the absolute configuration at the N atoms has been experimentally determined, compounds with the (*R*,*R*) configurations at the N atoms are, without exception, dextrorotatory at longer wavelengths. At least in the case of the mono-*N*-alkyldiaziridines, the observed sign of rotation at longer wavelengths may be due to the Cotton effect of the fourth transition, identified as $\pi^*_N \rightarrow 3s$.

The first two transitions of (*R*)-oxaziridine and (*R*)-*N*-methyloxaziridine have negative Cotton effects, as does the (2*R*,3*R*)-3-methyloxaziridine. The first transition of (2*S*,2*R*)-3-methyloxaziridine also has a negative CD, indicating that optical activity of oxaziridines is not dominated by the configuration at N.

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High-Resolution Optical Studies on *C*-Phycocyanin via Photochemical Hole Burning

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Abstract: We have shown that both the native *C*-phycocyanin and its corresponding free biline chromophore undergo reversible, low-temperature photochemistry. We attribute this photochemistry to reversible proton-transfer processes and utilize the observed photoreaction for photochemical hole burning (PHB). Using narrow-band PHB experiments, we have been able to perform high-resolution optical studies and show that the protein–chromophore assembly forms a very rigid structure. The results lead to the conclusion that the light-induced proton transfer occurs most probably in the triplet state.

Introduction

C-Phycocyanins (*C*-PC) are known to be the light-harvesting pigments of blue green and red algae.[1-4] The molecules contain the bile pigment chromophores, i.e., absorbers with high oscillator strength, which are covalently bound to large proteins. *C*-PC is composed of two protein subunits with molecular weights in the range of 2×10^4. It contains three chromophores, one in the α and two in the β subunit.

Conformational studies on *C*-phycocyanin have been performed with optical absorption spectroscopy.[5] These studies can be summarized as follows:

(a) The protein environment stabilizes certain chromophore configurations and thus reduces the optical line width of the bile pigment chromophores, which can (in their unstabilized forms) attain various configurations varying from cyclic porphyrin-type structures to elongated polyene-type structures. The coexistence of these configurations leads to a relatively large inhomogeneous bandwidth of the optical spectra of free bile pigments in the solid state or in liquid solution.[5,6]

(b) The most likely chromophore structure of native *C*-PC is an elongated polyene-type conformation which is characterized by a very strong optical absorption in the low-energy band (6000 Å) and by a weaker absorption in the near-UV region (3500 Å).[5,7-9]

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