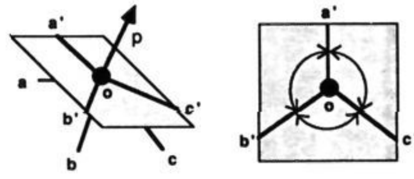
Scheme III



(iii) Corrections to MM. The molecular mechanics parameters for stretching, bending, torsions and van der Waals interactions involving one or more valence centers have in general been set equal to those of a sp^3 carbon atom. Exception is made only when the following situations are encountered.

(1) When a bond or planar angle includes at least one valence σ bond or a dihedral angle includes at least two valence σ bonds, their respective stretching, bending, or torsional constants are set equal to zero.

(2) When the anchor atom of a planar angle is a valence center, the value of the angle is replaced by the value of the *projected angle*. The MM parameters are not changed, only the definition of the angle. This *projected angle* is defined according to the Scheme III as the angle a′ob′ or b′oc′ or c′oa′ between the projection of the bonds (ao, bo, and co) onto the plane orthogonal to the vector p defined in Scheme I.

(3) When a dihedral angle includes one valence σ bond, the torsional constants are multiplied by a term Θ_{ij} whose value in turn depends on the value of the function $\Gamma_{ij} = c_{ipx}c_{jpx}\mathrm{Ex}_1(ij)$ (a function of the bond length r_{ij} and the orientation of p_i and p_j defined in Scheme AI). The form of Θ_{ij} is:

$$\Theta_{ij} = 0.85\left\{\left(1 + \frac{\tan^{-1}(4.0(2.0\Gamma_{ij} - \tfrac{1}{2}))}{\tan^{-1}(4.0)}\right) - \left(1 + \frac{\tan^{-1}(2.0)}{\tan^{-1}(4.0)}\right)\right\} \tag{A18}$$

Acknowledgment. This work was supported by the SERC (UK) under Grant No. GR/F 48029, 46452, and GR/G 03335. All ab initio computations were carried out using MC-SCF programs[18] that are available in GAUSSIAN 90.[19]

Registry No. Ergosterol, 57-87-4.

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The Nonplanar Amide Group in *N*-Acylaziridines: Conformational Behavior and Chiroptical Properties

G. V. Shustov,*,† G. K. Kadorkina,† S. V. Varlamov,† A. V. Kachanov,†
R. G. Kostyanovsky,† and A. Rauk*,‡

Contribution from the Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., 117977 Moscow, U.S.S.R., and Department of Chemistry, The University of Calgary, Calgary, Canada T2N 1N4. *Received June 10, 1991*

Abstract: Chiroptical properties in the intrinsically dissymmetric amide chromophore of *N*-acylaziridines are investigated experimentally and by ab initio molecular orbital calculations. Computations on *N*-formylaziridine (**1a**) and measurements of the CD spectra of (1*R*,2*R*)-1-acetyl-2-methylaziridine (**1b**), (1*R*,2*R*)-1-(α-hydrohexafluoroisobutyryl)-2-methylaziridine (**1c**), (2′*S*)-1-(2′-methylbutyryl)aziridine (**1d**), and (2′*S*)-1-(2′-methylbutyryl)-2,2-dimethylaziridine (**1e**) suggest that the Cotton effect (CE) for the long wavelength absorption (band I) obeys a spiral rule: a right-handed twist of the O═C—N—C(ring) bonds corresponds to a negative CE for band I. Band I is assigned to the valence n_O–π^*_{CO} transition. The next four higher energy absorptions are due to transitions to Rydberg states, n_N–3s and n_N–3p. Experimental CD spectra are also reported for the related compounds, (2′*S*)-1,2-bis(2′-methylbutyryl)-3,3-dimethyldiaziridine (**2a**), (α*S*)-1,2-diacetyl-3-*sec*-butyldiaziridine (**2b**), (2′*S*)-2-(2′-methylbutyryl)-3,3-dimethyloxaziridine (**3a**), (5*S*)-2-acetyl-5-methyl-1-oxa-2-azaspiro[2.5]octane (**3b**), (*S*)-*N*,*N*-dimethyl-2-methylbutyramide (**4**), and (2*S*)-1-(α-hydrohexafluoroisobutyryl)-2-methylazetidine (**5**).

Introduction

N-Acyl-substituted three-membered nitrogen heterocycles present a certain interest as compounds containing the most nonplanar amide group. The high degree of nonplanarity of such amides follows from the results of structural studies in the solid[1] and gaseous[2] phases, and is confirmed by the data of IR, ^{1}H NMR, and UV spectra in solution.[3] Nonplanarity and, connected with it, inherent chirality of the amide chromophore in *N*-acylaziridines strongly affect the circular dichroism (CD) spectra,[4] for the interpretation of which a correct assignment of optically active electronic transitions is required. Hitherto, assignments for the nonplanar amide chromophore are based only upon semiempirical calculations.[5] The experimental studies of the chiroptical

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* Author to whom correspondence should be addressed.

† Academy of Sciences of the U.S.S.R.

‡ The University of Calgary.

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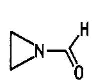
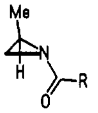
properties of this chromophore were mainly conducted on stereochemically rigid models, i.e., bi- and tricyclic lactams.[6] Unlike these compounds, the stereoisomers of *N*-acylaziridines can be interconverted by way of rotation around the N–C(O) bond and nitrogen inversion. The high stereochemical lability of the amide group in *N*-acylaziridines has been noted;[3a–d,4] however, there are no quantitative estimates of the rotation and inversion barriers.[7] Values of these barriers were obtained with the help of semiempirical calculations[2b,4,8] and by ab initio computation at the RHF/3-21G level.[8] The latter study, by Rademacher and Wurthwein (RW),[8] found that 1-formylaziridine exists in a chiral conformation, racemization being hindered by an unusually low barrier (1.4 kcal/mol) to pyramidal inversion at N.

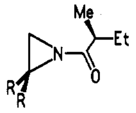
In the present work, ab initio calculations at a higher level of theory than RW[8] on the prototypical 1-formylaziridine (**1a**) are presented to elucidate the conformational behavior of the nonplanar amide group and the nature of its lowest excited singlet states. The calculated data are compared with the results of experimental investigations of the CD behavior of *N*-acylaziridines **1b–e**. In addition, we have investigated the CD spectra of even more nonplanar amides: N-acylated diaziridines **2a,b**, and oxaziridines **3a,b**, and also of amides **4** and **5**, in which the amide group is virtually planar.



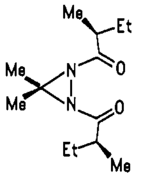
1a



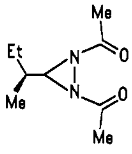
(1*R*,2*R*)-**1b** R = Me
(1*R*,2*R*)-**1c** R = $CH(CF_3)_2$



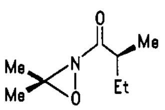
(2'*S*)-**1d** R = H
(2'*S*)-**1e** R = Me



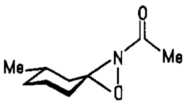
(2'*S*)-**2a**



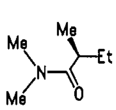
(α*S*)-**2b**



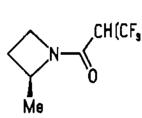
(2'*S*)-**3a**



(5*S*)-**3b**



(*S*)-**4**



(2*S*)-**5**

Theoretical Method

The geometry of 1-formylaziridine **1a** was fully optimized by Hartree–Fock SCF calculations at the 6-31G* level by using the GAUSSIAN 86 system of programs.[9] Stationary points corresponding to transition structures for rotation about the N–C(O) bond and pyramidal inversion at N were also located and their identities as transition structures confirmed by harmonic frequency analysis, which also provided corrections for zero-point vibrational energies (ZPVE). The effect of electron correlation on the barrier heights was checked by single-point recomputation of several of the structures by second-order Møller–Plesset perturbation theory (MP2).[10,11] For the purpose of determining the transition properties, the wave functions were redetermined in center-of-mass coordinates using the internal 6-31G basis set, augmented by addition of diffuse s and p functions to the basis sets of the C, N, and O atoms: $\alpha_C = 0.020$; $\alpha_N = 0.028$; $\alpha_O = 0.036$. Addition of the diffuse functions is required to describe the lowest few Rydberg states. The frontier orbitals are displayed as modified Jorgensen–Salem plots.[12]

The method used to calculate oscillator and optical rotatory strengths is the same as was used previously,[13–15] and has been described in detail elsewhere.[16] Partially correlated wave functions for the ground and excited states are determined to first order in Rayleigh–Schrödinger perturbation theory,

$$\psi_n = \psi_n^o - \Sigma_j a_{nj} \Phi_j^o \tag{1}$$

where

$$a_{nj} = \langle \psi_n^o | H | \Phi_j^o \rangle / (\langle \Phi_j^o | H | \Phi_j^o \rangle - \langle \psi_n^o | H | \psi_n^o \rangle) \tag{2}$$

H is the exact Hamiltonian, Φ_j^o is a singlet singly or more highly excited configuration derived from the Hartree–Fock determinant, Φ_{HF}, and ψ_n^o is a linear combination of strongly interacting Φ_l^o ($l \neq j$) selected from at most singly excited configurations. Thus, for the ground state, $\psi_o^o = \Phi_{HF}$. All configurations for which the interaction coefficient α_{nj} (eq 2) was greater than 0.03 were included in the zero-order part of the CI wave function. Electric dipole transition moments in the length $\langle r \rangle_{on}$ and velocity $\langle \nu \rangle_{on}$ formalism and magnetic dipole transition moments $\langle m \rangle_{on}$ are explicitly evaluated from

$$\langle r \rangle_{on} = \langle \psi_o | \mu | \psi_n \rangle \tag{3}$$

$$\langle \nu \rangle_{on} = \langle \psi_o | \nabla | \psi_n \rangle / (E_n - E_o) \tag{4}$$

$$\langle m \rangle_{no} = -i \langle \psi_n | \mathbf{m} | \psi_o \rangle \tag{5}$$

where the operators μ, ∇, and **m** have their usual definitions[16] and

$$E_n = \langle \psi_n | H | \psi_n \rangle \tag{6}$$

Oscillator strengths f_{on} are calculated by the "mixed" formalism

$$f_{on} = {}^2\!/_3 \langle \psi_o | \nabla | \psi_n \rangle \langle r \rangle_{no} \tag{7}$$

Optical rotary strengths are evaluated as

$$[\mathrm{R}_{on}]^r = \langle r \rangle_{on} \langle m \rangle_{no} \tag{8}$$

and in the origin independent form

$$[R_{on}]^\nu = \langle \nu \rangle_{on} \langle m \rangle_{no} \tag{9}$$

The extent of the deviation of $\langle r \rangle$ and $\langle \nu \rangle$ from collinearity and in

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magnitude is a measure of the quality of the wave function for the particular states and of the origin dependence of $[R]^r$.

Experimental Section

The CD spectra were measured on a JASCO J-500A spectropolarimeter with a DP-500N data processor, the UV spectra on a Specord UV-Vis spectrophotometer, the ^{1}H NMR spectra on a Bruker WM-400 spectrometer (400 MHz, from TMS), and the optical rotation angles on a Polamat A polarimeter.

(1*R*,2*R*)-1-Acetyl-2-methylaziridine (1b), (1*R*,2*R*)-1-(α-hydrohexafluoroisobutyryl)-2-methylaziridine (1c), and (2*S*)-1-(α-hydrohexafluoroisobutyryl)-2-methylazetidine (5) were prepared as previously described.[4]

(2′*S*)-1-(2′-Methylbutyryl)aziridine (1d). A solution of (*S*)-(+)-2-methylbutyryl chloride[17] (1.21 g, 10 mmol) in absolute Et_2O (10 mL) was added dropwise to aziridine (0.45 g, 10 mmol) and Et_3N (1.01 g, 10 mmol) in absolute Et_2O (20 mL) with cooling (−30 °C) and stirring. After 2 h at 20 °C the precipitate was filtered off and the solution was evaporated in vacuo. The residue was distilled, providing *N*-acylaziridine **1d** (0.91 g, 72%), bp 60 °C (7 mm), $[\alpha]^{20}_D$ +19.6° (*c* 1.9, heptane). Anal. Found: C, 66.2; H, 10.5; N, 10.8. Calcd for $C_7H_{13}NO$: C, 66.1; H, 10.3; N, 11.0. ^{1}H NMR in $CDCl_3$ (*J*, Hz): δ 0.89 ($MeCH_2$, ^3J = 7.5), 1.14 (MeCH, ^3J = 6.8), 1.47 and 1.72 (CH_AH_B, J_{AB} = 13.3), 2.20 (CH_2CH_2N), 2.52 (CH).

(2′*S*)-1-(2′-Methylbutyryl)-2,2-dimethylaziridine (1e) was obtained as described above: yield 54%, bp 68 °C (7 mm), $[\alpha]^{20}_D$ + 38.5° (*c* 1.2, heptane). Anal. Found: C, 69.5; H, 11.0; N, 8.9. Calcd for $C_9H_{17}NO$: C, 69.7; H, 11.0; N, 9.0. ^{1}H NMR in $CDCl_3$ (*J*, Hz): δ 0.93 ($MeCH_2$, ^3J = 7.5), 1.14 (MeCH, ^3J = 6.8), 1.32 and 1.34 (Me_2C), 1.49 and 1.73 (CH_AH_B, J_{AB} = 13.6), 2.10 and 2.14 (NCH_AH_B, ^2J < 0.5), 2.11 (CH).

(2′*S*)-1,2-Bis(2′-methylbutyryl)-3,3-dimethyldiaziridine (2a). A solution of (*S*)-(+)-2-methylbutyryl chloride (0.36 g, 3 mmol) in absolute Et_2O (5 mL) was added dropwise to 3,3-dimethyldiaziridine (0.11 g, 1.5 mmol) and Et_3N (0.35 g, 3.5 mmol) in absolute Et_2O (10 mL) with cooling (−78 °C) and stirring. After 0.5 h at 0 °C the precipitate was filtered off, the solution was evaporated in vacuo at 0 to +5 °C, and the product was extracted from the residue with cold pentane. After removal of pentane, 0.28 g (78%) of *N*,*N*′-diacyldiaziridine **2a** was obtained. This product was identified by ^{1}H NMR and CD spectra (Figure 3, Table II). ^{1}H NMR in $CDCl_3$ (*J*, Hz): δ 0.94 ($MeCH_2$, ^3J = 7.3), 1.18 (MeCH, ^3J = 7.1), 1.49 (Me_2C), 1.49 and 1.76 (CH_AH_B, J_{AB} = 13.7), 2.52 (CH).

(α*S*)-1,2-Diacetyl-3-*sec*-butyldiaziridine (2b). (2*S*,4*S*,6*S*)-2,4,6-Tri-*sec*-butyl-1,3,5-triazabicyclo[3.1.0]hexane (TABH)[15] (0.93 g, 3.7 mmol) and H_2NOSO_3H (1.24 g, 11 mmol) in 2 N H_2SO_4 (20 mL) was stirred at 40 °C (until the dissolution of TABH). The reaction mixture was washed with Et_2O and neutralized with 40% aqueous solution of KOH upon cooling (5–10 °C). The cold solution was saturated with KOH pellets and product extracted with CH_2Cl_2 and dried over K_2CO_3. After the solvent removal the residue was distilled in vacuo, providing 0.2 g (54%) of (α*S*)-3-*sec*-butyldiaziridine (SBD), bp 100 °C (85 mm), $[\alpha]^{20}_D$ + 10.4° (*c* 0.5, heptane). Anal. Found: C, 60.2; H, 12.1; N, 27.8. Calcd for $C_5H_{12}N_2$: C, 60.0; H, 12.0; N, 28.0. A solution of acetyl chloride (0.28 g, 3.6 mmol) in absolute Et_2O (5 mL) was added dropwise to SBD (0.15 g, 1.5 mmol) and Et_3N (0.36 g, 3.6 mmol) in absolute Et_2O (10 mL) with cooling (−78 °C) and stirring. After 0.5 h at 20 °C the precipitate was filtered off, the solution was evaporated in vacuo, and the product was extracted from residue with pentane. After removal of pentane, 0.17 g (63%) of *N*,*N*′-diacetyldiaziridine **2b** was obtained. This product was identified by ^{1}H NMR and CD spectra (Table II). ^{1}H NMR in $CDCl_3$ (*J*, Hz): δ 0.97 ($MeCH_2$, ^3J = 7.3), 1.12 (MeCH, ^3J = 7.1), 1.27 (CH, broad signal), 1.38 (CH_A, J_{AB} = 13.4), 1.76 (CH_B, ^3J = 4.2), 2.24 and 2.25 (MeCO), 3.56 (CHN_2, ^3J = 8.3).

(2′*S*)-2-(2′-Methylbutyryl)-3,3-dimethyloxaziridine (3a) was obtained from acetone and (*S*)-(+)-2-methylbutyryl chloride by analogy with 2-benzoyl-3,3-pentamethyleneoxaziridine:[18] yield 39%, bp 75–76 °C (10 mm), $[\alpha]^{20}_D$ +6.5° (*c* 3.7, heptane). Anal. Found: C, 61.0; H, 9.8; N, 8.7. Calcd for $C_8H_{15}NO_2$: C, 61.1; H, 9.6; N, 8.9. ^{1}H NMR in C_6D_6 (*J*, Hz): δ 0.82 ($MeCH_2$, ^3J = 7.3), 1.02 (MeCH, ^3J = 7.0), 1.12 (Me_2C), 1.37 and 1.72 (CH_AH_B, $^3J_{AB}$ = 14.3), 2.44 (CH).

(5*S*)-2-Acetyl-5-methyl-1-oxa-2-azaspiro[2.5]octane (3b) was obtained from (3*S*)-(−)-3-methylcyclohexanone ($[\alpha]^{20}_D$ −13.0°, neat) and acetic anhydride as previously described for 2-acetyl-3,3-pentamethyleneoxaziridine:[18] yield 30%, bp 71–73 °C (1 mm), $[\alpha]^{20}_D$ +0.9° (*c* 7.3, heptane). Anal. Found: C, 63.7; H, 9.0; N, 8.1. Calcd for $C_9H_{15}NO_2$: C, 63.9; H, 8.9; N, 8.3. ^{1}H NMR in $CDCl_3$ (*J*, Hz): δ 0.96 (MeCH, ^3J = 6.8), 1.00 (6-H_a, ^2J = 12.2, $^3J_{aa}$ = 13.9, $^3J_{ae}$ = 3.5), 1.40 (4-H_e, 8-H_e, broad signal), 1.61 (7-H_a, ^2J = $^3J_{aa}$ = 13.3, $^3J_{ae}$ = 4.3), 1.67 (4-H_a, ^2J = 13.6, $^3J_{aa}$ = 12.0), 1.78 (6-H_e), 1.79 (5-H_a), 1.88 (7-H_e), 1.94 (8-H_a, ^2J = $^3J_{aa}$ = 13.3, $^3J_{ae}$ = 4.3), 2.17 (MeCO).

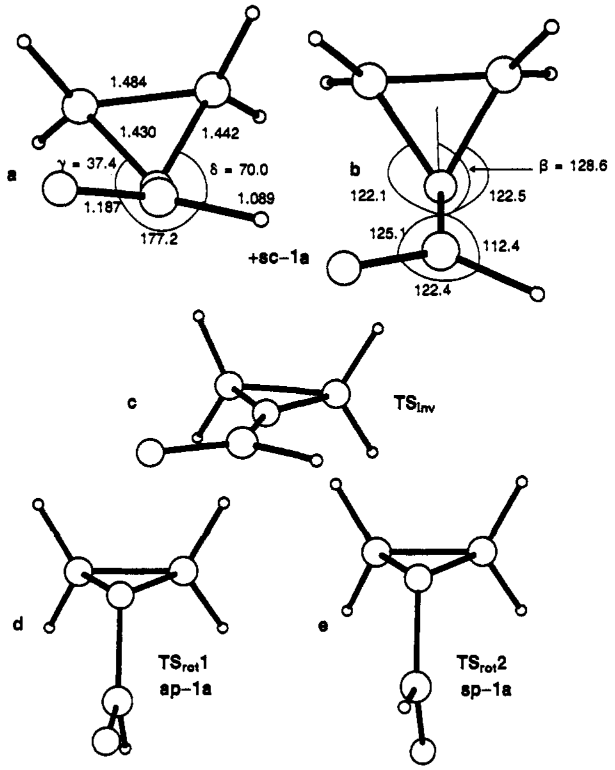

Figure 1. The 6-31G* structures of the +*sc* rotamer of 1-formylaziridine **1a** (a, b), the transition state for inversion TS_{inv} (c), and the transition structures for rotation, $TS_{rot}1$ or *ap*-**1a** (d), and $TS_{rot}2$ or *sp*-**1a** (e) (distances in Å, angles in deg).

(*S*)-*N*,*N*-Dimethyl-2-methylbutyramide (4). A solution of (*S*)-(+)-2-methylbutyryl chloride (1.21 g, 10 mmol) in absolute Et_2O (10 mL) was added dropwise to dimethylamine (1.35 g, 30 mmol) in absolute Et_2O (20 mL) with cooling (−30 °C) and stirring. After 2 h at 20 °C the precipitate was filtered off and the solution was evaporated in vacuo. The residue was distilled, providing amide **4** (1.14 g, 88%), bp 67 °C (7 mm), $[\alpha]^{20}_D$ +37.8° (*c* 1.9, heptane). Anal. Found: N, 10.75. Calcd for $C_7H_{15}NO$: N, 10.8. ^{1}H NMR in $CDCl_3$ (*J*, Hz): δ 0.86 ($MeCH_2$, ^3J = 7.6), 1.07 (MeCH, ^3J = 6.8), 1.38 and 1.67 (CH_AH_B, J_{AB} = 13.3), 2.94 and 3.03 (Me_2N).

Results and Discussion

Typical amide features include planarity or near-planarity of the configuration at N, coplanarity of the N and acyl moieties, and high rotational barriers about the N–C(O) bond. All of these features are attributed to the two-electron–two-orbital n_N–π^*_{CO} stabilizing interaction. By contrast, the fully optimized structure of 1-formylaziridine **1a** (Figure 1) is characterized, firstly, by the high degree of pyramidality of the nitrogen atom and the consequent nonplanarity of the amide group as a whole; the out-of-plane angle, β, of the N–C(O) bond is 128.6°. Secondly, the optimized structure exhibits an *intrinsic* chirality of the amide group, the most stable structure is the asymmetric *syn*-clinical rotamer ±*sc*-**1a** (dihedral angle C—N—C═O, γ, is equal to ±37.4°) (Figure 1, Scheme I). Both anomalous features (for amides) are observed experimentally in related systems, for 1-*p*-bromobenzoylaziridine in a crystal (β = 122°, γ = ±49°)[1a] and 1-acetylaziridine in the gas phase (β = 118°, γ = ±24°).[2b] The asymmetry of the two dihedral angles that the acyl group makes with the N–C bonds of the ring, γ = 37.4° and δ = 70.0° (Figure 1), also is significant in understanding the conformational possibilities in *N*-acylaziridine systems. While the $n_N \cdots \pi^*_{CO}$ interaction is dominant, the acyl group is twisted away from the optimum orientation for this interaction (i.e., γ = δ) to a geometry which permits one of the strained ring C–N bonds to act as an additional donor to the π^*_{CO} orbital (δ approaches 90°). The equilibrium structure is a compromise between the two attractive

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Table I. Stationary Structures of 1-Formylaziridine **1a**

structure	E(RHF), au	E_{rel}, kcal/mol	E(MP2), au	E_{rel}, kcal/mol	ZPVE, kcal/mol	total E_{rel}, kcal/mol
equil'm (±*sc*)	−245.777 281	0.0	−246.514 230	0.0	54.34	0.00
TS_{inv}	−245.767 542	6.11	−246.504 158	6.32	54.01	5.99
$TS_{rot}1$ (*ap*)	−245.765 730	7.24	−246.503 220	6.91	53.82	6.39
$TS_{rot}2$ (*sp*)	−245.771 142	3.85		~3.5		~3.1

Scheme I

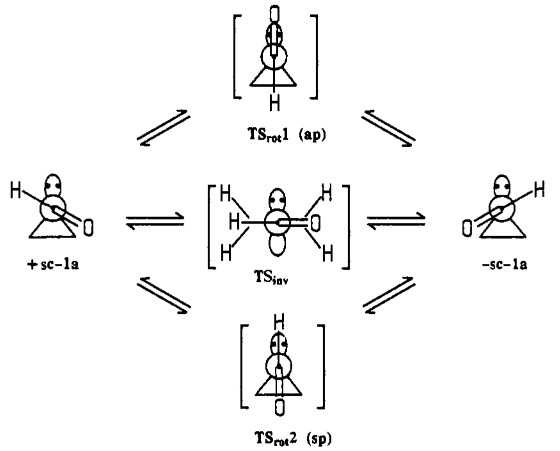

Table II. CD Spectra of Amides **1–5**[a]

compd	solvent[b]	band I (n_O–π^*_{CO} transition)	others[c]
(1*R*,2*R*)-**1b**	H	247 (1.037)	212 (0.515), 200n
	M	237 (1.415)	217s (0.708), 195s (−5.56)
(1*R*,2*R*)-**1c**	H	251 (1.983)	202 (−10.744)
	M	243 (1.402)	201 (−6.745)
(2′*S*)-**1d**	H	274 (0.01)	243 (−0.026), 212 (−0.02), 200p
	M	240 (−0.63)	199 (2.303)
(2′*S*)-**1e**	H	248 (−0.717)	200s (5.36)
(2′*S*)-**2a**	H	258 (−1.338)	205 (2.02)
(α*S*)-**2b**	H	253 (1.313)	200n
	M	248 (0.758)	205n
(2′*S*)-**3a**	H	266 (−1.273)	200p
	M	259 (−1.444)	200p
(5*S*)-**3b**	H	263 (−0.737)	200p
(*S*)-**4**	H	228 (−0.489)	204 (1.84)
	M	223 (−0.55)	200s (2.04)
(2*S*)-**5**	H	238 (0.543)	207 (−2.38)
	M	235 (0.583)	207 (−1.248)

[a] Wavelengths of apparent maxima in nm, $\Delta\epsilon$ values in parentheses. [b] H, *n*-heptane; M, methanol. [c] s, shoulder; n and p negative and positive CD but without a maximum.

Table III. Electronic States and Transition Properties for +*sc* Rotamer of 1-Formylaziridine **1a**[a]

state	description[b]	$[R]^{r\,c}$	$[R]^{v\,c}$	f	E (eV)	$\langle r^2\rangle^d$
1	M018–π^*_{CO}(n_O–π^*_{CO})	−14.1	−3.8	0.0049	6.10	11.5
2	M019–3s (Rydberg)	+3.4	+2.4	0.0012	8.16	63.2
3	M019–3p (Rydberg)	+8.4	+6.8	0.0489	8.39	57.1
4	M019–3p (Rydberg)	−0.4	−0.5	0.0010	8.64	69.7
5	M019–3p (Rydberg)	−6.3	−4.5	0.0029	8.85	76.0

[a] See Figure 1 for geometry; properties in this table calculated with the 6-31G + diffuse s, p basis (see text). [b] See Figures 5 and 6. [c] 10^{40} cgs. [d] Average size of the "upper" orbital, in units of bohr^2; see Figure 6.

interactions, with the first dominating the second. The relative importance of the N–C bond donors is reflected in the relative lengths of the two C–N bonds. The bond which is in a more favorable orientation to transfer electron density to the π^*_{CO} orbital is significantly longer than the other (1.442 Å versus 1.430 Å, Figure 1). In an unsymmetrically substituted aziridine ring, whether the +*sc* or the −*sc* rotamer dominates may be determined by electronic factors having to do with the substituent's effect on the donor ability of the C–N bond, as well as the more obvious steric factors. For instance, alkyl substitution at the 2-position would render the N–C_2 bond a better donor and, as a consequence, favor the *sc* conformer which places that bond as close to the perpendicular position relative to the plane of the acyl group as possible.

The achiral rotamers, *anti*-periplanar *ap*-**1a** and *syn*-periplanar *sp*-**1a**, are transition states, $TS_{rot}1$ and $TS_{rot}2$, respectively (Scheme I, Table I) for rotation about the N–C(O) bond. Both are stabilized by the interaction of the low-lying w_1 Walsh orbital of the three-membered ring[19] with the π^*_{CO} orbital. It is interesting to compare the conformational behavior of 1-formylaziridine **1a** with that of its carbocyclic analogue, formylcyclopropane.[20] In the case of the latter only the w–π^*_{CO} interaction[20b] is realized and, according to calculations at the 6-31G* level, rotamers *ap* and *sp* are the ground states of the rotation process and the *sc* rotamer is the transition state.[20a] Noteworthy also is the great difference in energies of the *sp* and *ap* rotamers of 1-formylaziridine **1a** (3.3 kcal/mol) as compared to the difference of the respective rotamers of formylcyclopropane (0.3 kcal/mol).[20a] The greater relative stability of the *sp* rotamer of **1a** is evidently due to the interaction of anti-periplanar n_N and σ^*_{CO} orbitals and perhaps also a dipole–dipole interaction of the three-membered ring with C=O bond. In the case of formylcyclopropane the first of these interactions is absent and the second one is expressed to a lesser degree, since unlike the aziridine ring, which possesses a permanent dipole moment, the cyclopropane ring is essentially nonpolar.

The interconversion of +*sc* and −*sc* enantiomers may take place by means of rotation around the N–C(O) bond, and also by inversion through the planar transition state, TS_{inv} (Scheme I). However, the calculated inversion barrier turns out to be somewhat higher than the rotation barrier through the lower rotational transition state, $TS_{rot}2$ (sp rotamer) (Table I). The calculated data (Table I) testify to the fact that there is a weakening of the amide "resonance" upon introduction of the nitrogen atom of the amide group into a strained three-membered ring. The calculated barrier to N–C(O) rotation, ~3 kcal/mol, is much less than more typical values, e.g., ~18 kcal/mol in the case of *N*,*N*-dimethylformamide.[21] Moreover, the ground-state configuration of the nitrogen atom is strongly pyramidal, although the inversion barrier is much lower than normally found in aziridines.[22] In the sequence, *N*-acyl-substituted aziridines, diaziridines, and oxaziridines, the rotation barrier will decrease and the inversion barrier will increase. The latter was shown previously in the case of *N*-carbamoyl derivatives.[3] The high stereochemical lability of the nonplanar amide group in *N*-acylaziridines must lead to the fact that the intrinsic enantioselectivity (preference for one *sc* conformer over the other) of this group will depend on a chiral environment. At the same time it is known that the Cotton effect (CE) sign of the long-wavelength absorption band in the CD spectrum of the nonplanar amide chromophore is determined by its intrinsic chirality.[6a–c] If the equilibrium has significant populations of both forms, the observed CE will be that of the dominant form and should be temperature or solvent dependent. If the dihedral angle (γ or δ) is sufficiently different, the wavelengths

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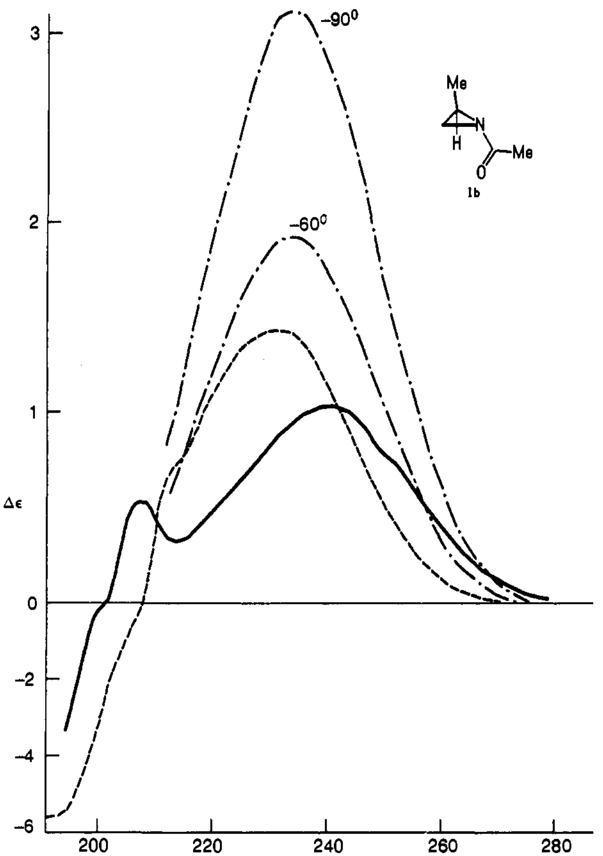


Figure 2. The CD spectra of *N*-acylaziridine **1b** in heptane (—) and in MeOH (---) at 20 °C; in EPA (-·-) at different temperatures.

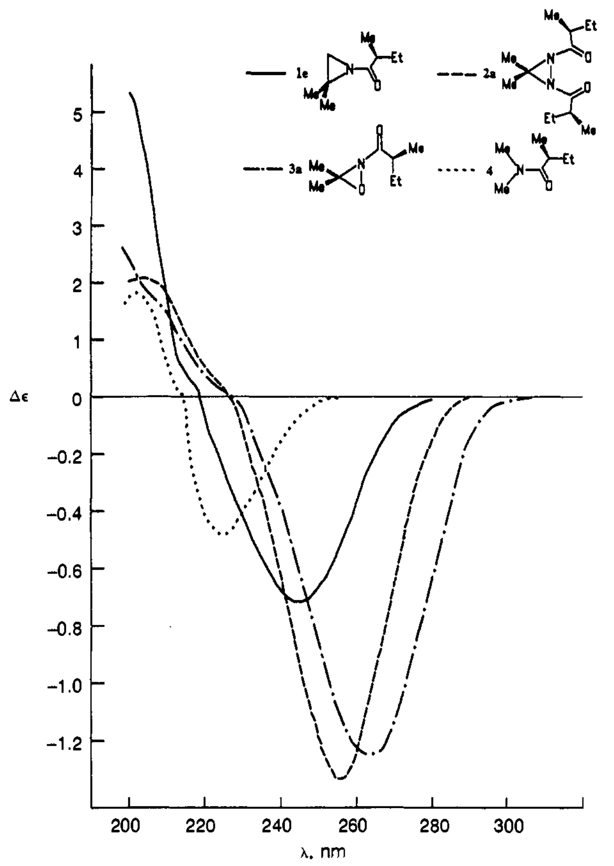


Figure 3. The CD spectra of *N*-acyl-substituted aziridine **1e** (—), diaziridine **2a** (---), oxaziridine **3a** (-·-), and dimethylamine **4** (···) in heptane.

of the n_O–π^*_{CO} absorption may also be sufficiently different to result in a bisignate form for this band. Consequently, from the CD spectra of *N*-acylaziridines, it is possible to judge about the detailed chirality of the nonplanar amide group proper, and its environment.

In the CD spectra of *N*-acyl-substituted three-membered heterocycles **1b–e–3a,b**, two intense bands of opposite signs are characteristic features (Table II, Figures 2–4). The calculation of the lowest excited singlet states of the nonplanar amide chromophore itself in 1-formylaziridine **1a** also gives two first CEs with opposite signs (Table III), and the difference in wavelength (51 nm) corresponds to the observed value (~50 nm) for *N*-acylaziridines **1b–e**. The hypsochromic shift of the long-wavelength band I when heptane is substituted for protic solvents (MeOH or EPA (ethanol–isopentane–ether, 2:5:5), Figure 2) testifies to the participation of the electrons of a nonbonding orbital in the first transition. According to the calculation, this is the n orbital of the oxygen atom, which is the principal contributor to the second occupied MO (MO18, Figure 5a). Electronic transition is to the antibonding π^*_{CO} orbital (Figure 6a,b). The HOMO electrons (mainly n_N orbital) participate in a Rydberg n_N–3s transition and give rise to the second intense dichroic absorption band in the CD spectra of *N*-acylaziridines **1b–e**. The next three lowest excited states of **1a** are also determined as Rydberg states (Table III, Figure 6). In contrast to the present results, previous studies, based on semiempirical calculations of the nonplanar amide chromophore, have ascribed the first transition (band I) to n_N–π^*_{CO}, and the short-wavelength band (at ~200 nm) to a π–π^* transition.[5]

For *N*-acylaziridines **1b,d**, a comparatively weak CE at 212–217 nm of the same sign as the CE of n_O–π^*_{CO} transition (Table II, Figures 2 and 4) is also observed. As found with other nonplanar amides,[6c] this CE is, by all appearances, the result of self-association, since it disappears upon dilution. The present calculations on 1-formylaziridine **1a** do not suggest an alternative explanation for the presence of this band.

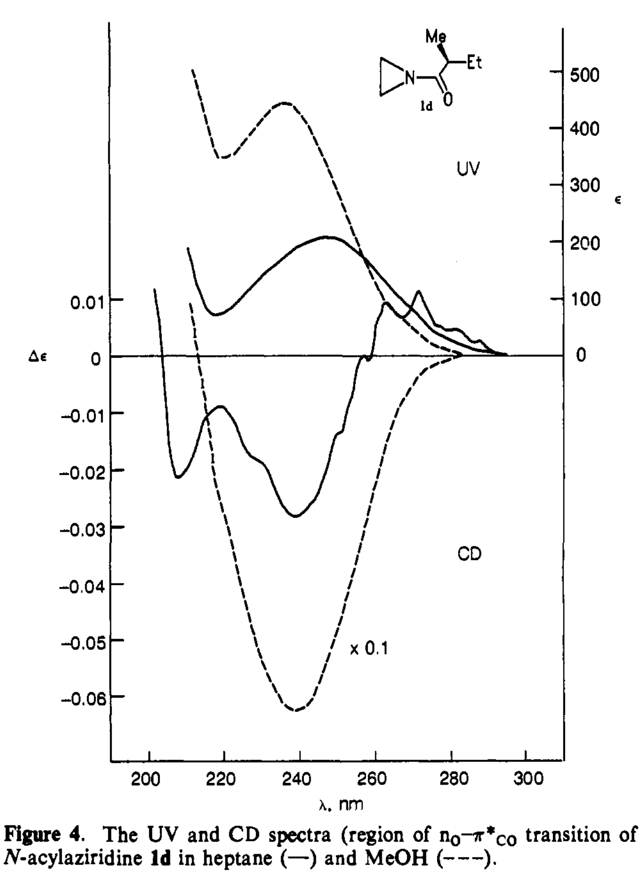


Figure 4. The UV and CD spectra (region of n_O–π^*_{CO} transition of *N*-acylaziridine **1d** in heptane (—) and MeOH (---).

The weakening of amide conjugation at the expense of increasing the degree of pyramidality of nitrogen atom (the di-

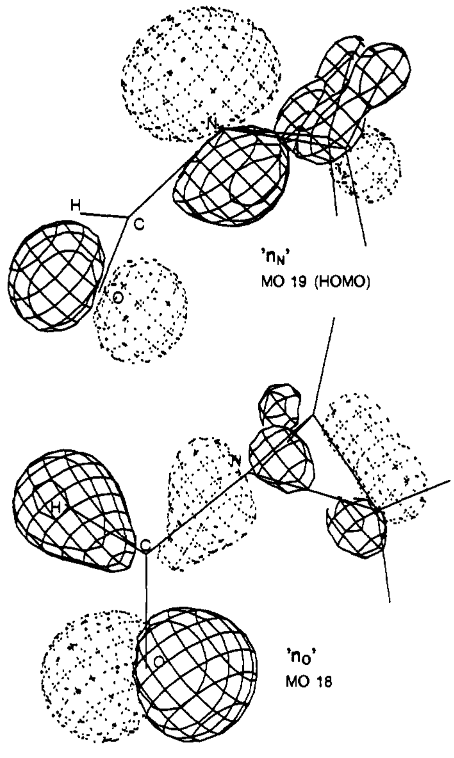


Figure 5. The two upper occupied MOs involved in the electronic transitions of 1-formylaziridine **1a**, contour values 0.075.

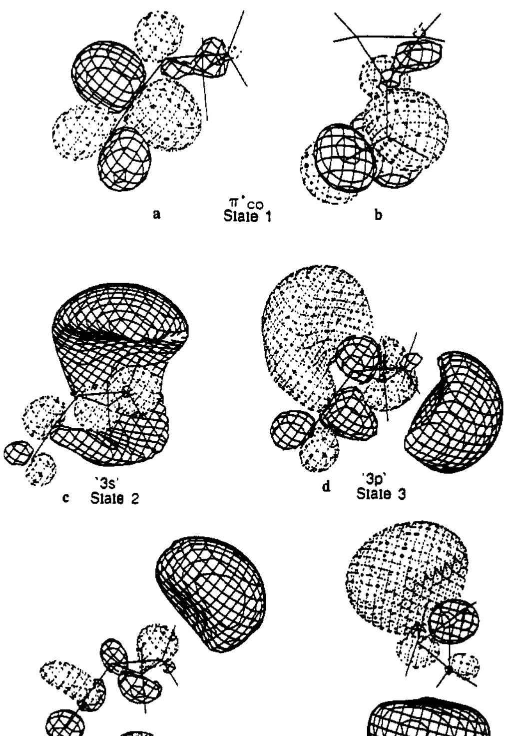


Figure 6. The terminal orbitals of the lowest excited singlet states of 1-formylaziridine **1a**: (a, b) first excited single state, contour value 0.05; (c–f) Rydberg orbitals of the next four singlet states reduced in scale by 0.75, contour values 0.024.

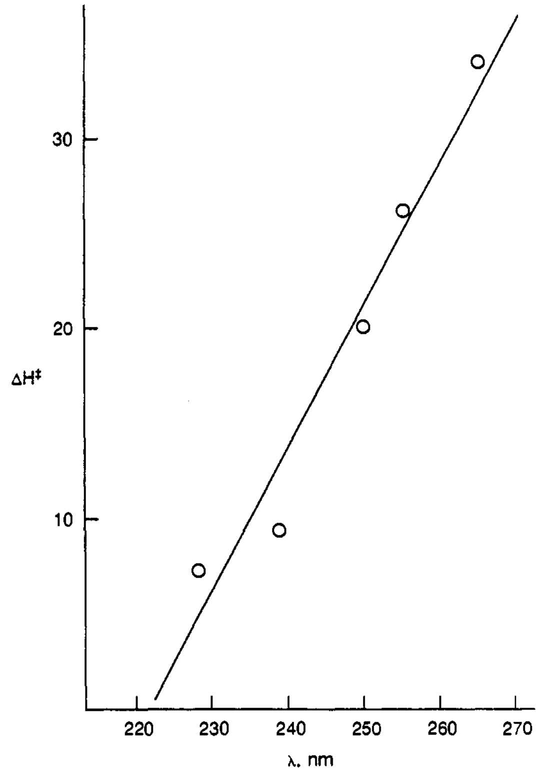
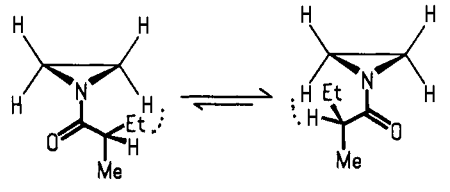


Figure 7. Graph $\Delta H^{\ddagger}$ versus λ_{max} values (correlation of 0.981, slope of 0.78; see text).

Scheme II



-sc-1d +sc-1d

minishing of p character of the n_N orbital) must lead to a narrowing of the HOMO–LUMO energy gap and therefore to a bathochromic shift of the dichroic absorption bands, the electronic transitions of which are connected with these orbitals. Such a conclusion has been previously reached on the basis of quantum chemical calculations.[5] It is experimentally shown in the present work. The wavelength maxima of band I in the CD spectra of *N*-acyl derivatives (Table II) are observed to increase in the series:

$$\text{dimethylamide } \mathbf{4} < \text{azetidine } \mathbf{5} < \text{aziridines } \mathbf{1b\text{–}d} \ll \text{diaziridines } \mathbf{2a,b} < \text{oxaziridines } \mathbf{3a,b}$$

Evidently, the p character of the n_N orbital and its ability to participate in amide conjugation decrease in the same order. The observed linear correlation of λ_{max} of band I of amides **1–5** with the lowering in barriers of nitrogen inversion ($\Delta H^{\ddagger}$) of the *N*-acyl amides relative to structurally related *N*-alkyl derivatives of amines is additional confirmation: for dimethylamide **4**–*N*-methyl-*N*,*N*-dibenzylamine, $\Delta H^{\ddagger}$ = 7.2 kcal/mol;[22b] for *N*-acylazetidine **5**–1,3,3-trimethylazetidine, 9.1;[22b] for *N*-acylaziridines **1b–e**–1,2,2-trimethylaziridine, 20.2;[22b] for *N*,*N*′-diacyldiaziridines **2a,b**–1,3,3-trimethyldiaziridine, 26.7;[23] for *N*-acyloxaziridines **3a,b**–2,3-dimethyl-3-benzyloxaziridine, 34.1.[22b] The correlation is shown in Figure 7. It is known that the increase of inversion barriers in the indicated pair is ultimately related to the decrease of p character of the n_N orbital. It should be noted that in accordance with our assignment (Table III) the bathochromic shift of band I with the weakening of amide conjugation is mainly a consequence of a decrease of the LUMO (π^*_{CO}) energy, while in the other bands it is connected with the increase of HOMO (n_N) energy.

The greatest bathochromic shift of band I would be expected for an orthogonal orientation of the n_N and π^*_{CO} orbitals, as occurs in the *ap* and *sp* rotamers (Scheme I). Distortion of the equilibrium geometry toward the *sp* rotamer geometry as a conse-

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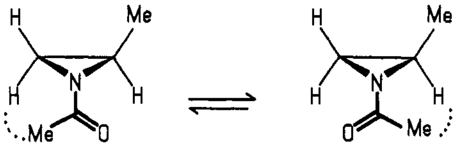
Table IV. The Temperature Dependence of the Optical Rotary Strength of the n–π^* Transition of *N*-Acylaziridines **1b–e** and Planar Amide **4** in EPA

	$[R_0^T]^a$				
T, K	**1b**	**1c**	**1d**	**1e**	**4**
293	2.73	5.42	−1.30	−3.24	−1.39
273	3.09	5.99	−1.57	−3.61	−1.57
243	4.05	7.17	−1.96	−4.55	−2.00
213	5.99	9.32	−3.48	−5.66	−2.70
183	9.40	12.40	−6.83	−7.60	−3.84
153	17.85	18.85	−17.84	−12.42	−5.00
A^b	−1.1 ± 0.1	0.33 ± 0.07	−2.7 ± 0.4	−0.3 ± 0.1	−2.8 ± 0.6
B^b	607 ± 18	400 ± 14	847 ± 80	424 ± 24	1193 ± 118
r^c	0.9998	0.9997	0.9977	0.9992	0.9975

[a] $[4R_0^T] \approx (1.08 \times 10^{40})R_0^T$ (CGSE). [b] *A* and *B* are coefficients of equations: $\ln [R_0^T] = A + B/T$ for **1b–e** and $[R_0^T] = A + B/T$ for **4**; error is for 95% confidence limits. [c] Correlation coefficient.

Scheme III

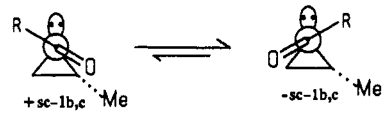


+sc-**1b** −sc-**1b**

quence of steric interactions with substituents or an attempt to minimize polarity in a medium of low dielectric constant should also result in a bathochromic shift of band I. Conversely, distortion in the opposite direction may increase the n_N–π^*_{CO} interaction, thereby raising the LUMO and causing a hypsochromic shift in band I. These considerations suggest an explanation for the bisignate form of band I in the CD spectrum of *N*-acylaziridine **1d** in heptane (Figure 4). The simplest explanation is that it is the result of a near cancellation of oppositely signed CEs, a dominant negatively signed CE at shorter wavelength, and a minor positively signed CE at longer wavelength. Both are due to band I of two conformers in which the intrinsic chirality is opposite (Scheme II). The −*sc* conformer is destabilized by an extra steric interaction of the ethyl group. Relief of this interaction is accompanied by distortion of the geometry toward the *sp* rotamer geometry. This distortion is compounded in nonpolar hexane since the molecular dipole moment is also minimized in the process. Change of solvent to methanol or EPA has the opposite effect with respect to the molecular dipole moment, thus countering the distortion which results in the bathochromic shift. In methanol, the bisignate character of band I is not observed (Figure 4). The observed signs of the CEs of the major and minor components are consistent with the model calculations on **1a**.

The stereochemical lability of the nonplanar amide group in *N*-acylaziridines **1b–e** is confirmed by strong temperature dependence of the rotatory strength of the n_O–π^*_{CO} transition (Table IV, Figure 2) in each case. A component of the low-temperature CE of *N*-acylaziridines **1d**,**e**, as in the case of dimethylamide **4**, is probably due to the preferential population of one or more of the rotamers of the chiral CH(Me)Et group. A two-position equilibrium (similar populations of both forms), associated with rotation around the amide N–C(O) bond, is certain for 1-acyl-2-methylaziridines **1b**,**c**. In **1b** and **1c**, there will be a strong thermodynamic preference for the 1,2-trans isomer, which presents two sterically similar C–H bonds for steric interaction with the acyl group (Scheme III). As discussed above, the presence of the methyl group at the 2-position of the ring will make the proximal N–C bond a somewhat better electron donor than the other. There is expected to be a slight stereoelectronic preference for that conformer which places this N–C bond in a better position to interact with the acyl π^* orbital. The involvement of this bond in conjugation with the π^* orbital is evident in the plot of the receiving orbital for the first transition, shown in Figure 6b. In the case of **1b** and **1c**, the stereoelectronically preferred conformer is −*sc*, which, according to the model calculations on **1a**, will have a (+)*ve* CE for band I (see Scheme IV). However, unlike the carbocyclic analogue (1*S*,2*S*)-*trans*-1-acetyl-2-methylcyclopropane,[24] in *N*-acylaziridines **1b**,**c** there is no linear dependence of the rotatory strength $[R_0^T]$ of the n_O–π^*_{CO} transition on $1/(1 + \exp(-\Delta G^0/RT))$ in the temperature range of 293–153 K as expected for a simple two-component equilibrium. In fact, the observed temperature dependence is logarithmic (Table IV). The most likely explanation is that at the higher temperatures (e.g., 293 K), the ratio of +*sc* and −*sc* rotamers of these *N*-acylaziridines is close to unity. In this case the intrinsic rotatory strengths compensate each other, and a large component of the (+)*ve* CE observed is due to a temperature-insensitive asymmetric perturbation of the chromophore by the chiral environment. Increasing population of the −*sc* rotamer as the temperature is lowered would account for the increased (+)*ve* CE and also for the logarithmic dependence on temperature.[25] Consequently, one fails to estimate the rotatory strengths of the individual +*sc* and −*sc* rotamers.

Scheme IV



+sc-**1b**,**c** -sc-**1b**,**c**

The Spiral Rule for Amides. A correlation of the CE sign of the n–π^* transition with the intrinsic chirality of nonplanar amide chromophores was found previously on the basis of an experimental study of the chiroptical properties of bi- and tricyclic lactams[6] and also quantum chemical calculations of the simplest models of this chromophore.[5] It was established that for nonplanar amides with a *positive* dihedral angle O═C—N—C (which corresponds approximately to the +*sc* rotamer of *N*-acylaziridines (Figure 1)), a *negative* CE is observed. The opposite is true for a negative dihedral angle (−*sc* rotamer) in which case a positive CE is observed. According to our calculation of 1-formylaziridine **1a**, this rule is also valid for *N*-acylaziridines. The calculated rotatory strength of the n_O–π^*_{CO} transition of +*sc* rotamer **1a** is negative (Table III). Thus, the indicated spiral rule predicts the energy preference of +*sc* rotamer for (2′*S*)-1-(2′-methylbutyryl)aziridines **1d**,**e** and the −*sc* rotamer for (1*R*,2*R*)-1-acyl-2-methylaziridines **1b**,**c**. Both assignments are reasonable on the basis of steric and electronic features, as discussed above.

Application of the spiral rule to *N*-acyloxaziridine **3a**,**b** and *N*,*N*′-diacyldiaziridines **2a**,**b**, is not justified at this point, since the influence of the α-heteroatom on the CE sign of n_O–π^*_{CO} transition in nonpolar amide chromophore is unknown. Moreover, fragment –C(O)–N–N–C(O)– in *N*,*N*′-diacyldiaziridines should be considered as single chromophore similar to other *N*,*N*′-diacylhydrazines.[26] The connection of the stereochemistry of such a chromophore with the sign of long-wavelength CE is yet to be determined. Indeed, for the close analogue (1*R*,2*S*)-*trans*-1-acetyl-2-methoxycarbonylaziridine, containing fragment –C(O)–N–C–C(O)–, the sign of long-wavelength CE is opposite to the sign determined according to the spiral rule.[4] In the CD spectra of three-membered nitrogen heterocycles, the anomalous behavior of aziridines and diaziridines with vicinal polar groups has already been reported.[13] Investigations into the optical activity

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(24) Tocanne, J. F. *Tetrahedron* **1972**, *28*, 389–416.

(25) At the suggestion of a referee, the preceding discussion was checked by further computation. The geometries of +*sc*-**1b** and −*sc*-**1b** were optimized at the STO-3G level of theory and improved estimates of the relative energies derived by single point computations with the 6-31G* basis set. The results are *E* (hartrees, RHF/STO-3G//STO-3G), *E* (hartrees, RHF/6-31G*//STO-3G), $\gamma°$, $\delta°$: +*sc*-**1b** −319.809 315, −323.855 096, 28.5, 86.8; −*sc*-**1b** −319.809 422, −323.855 336, 26.5, 88.8. Thus, the calculations support a slight preference of −*sc*-**1b** over +*sc*-**1b** by 0.15 kcal/mol (6-31G*). Assuming $\Delta S° = 0$ and no selective solvent interactions, the predicted Boltzman populations are (−*sc*-**1b**:+*sc*-**1b**): 293 K 0.56:0.44, 153 K 0.62:0.38. At present it is not possible to perform reliable calculations of optical rotatory strengths on **1b** directly.

(26) Overberger, C. G.; Montaudo, G.; Sebenda, J.; Veneski, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 1256–1258.

of these related chromophores are in progress and will be reported in due course.

Registry No. 1a, 45358-43-8; (1*R*,2*R*)-**1b**, 123620-68-8; (1*R*,2*R*)-**1c**, 123620-69-9; (2′*S*)-**1d**, 138385-63-4; (2′*S*)-**1e**, 138385-64-5; (2′*S*)-**2a**, 138385-65-6; (α*S*)-**2b**, 138385-67-8; (2′*S*)-**3a**, 138385-68-9; (5*S*)-**3b**, 138385-69-0; (*S*)-**4**, 138385-70-3; (2*S*)-**5**, 123557-05-1; TABH, 126503-75-1; SBD, 138385-66-7; H_2NOSO_3H, 2950-43-8; (*S*)-(+)-2-methylbutyryl chloride, 27763-54-8; aziridine, 151-56-4; 2,2-dimethylaziridine, 2658-24-4; 3,3-dimethyldiaziridine, 4901-76-2; acetone, 67-64-1; dimethylamine, 124-40-3; (3*S*)-(−)-3-methylcyclohexanone, 24965-87-5.

Conformationally Dependent Heavy Atom Effect of Chlorine on Alkene Triplet Lifetimes. Experimental and ab Initio Calculations

Richard A. Caldwell,*[1] Lance D. Jacobs,[1] T. R. Furlani,[2] E. Ann Nalley,[1,3] and J. Laboy[1]

Contribution from the Chemistry Program, BE 26, The University of Texas at Dallas, Richardson, Texas 75083-0688, and Calspan Advanced Technology Center, Buffalo, New York 14225. *Received June 27, 1991*

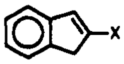
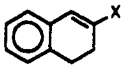
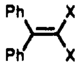
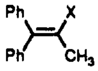
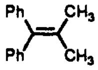
Abstract: The heavy atom effect of vinyl Cl in enhancing ISC rates of arylalkene triplets is shown to be much greater for substrates which can access nonplanar conformations. The experimental results are consistent with ab initio calculations of spin–orbit coupling.

Atoms of relatively high atomic number, when present in a molecule or in a solvent, cause enhanced rates of singlet–triplet or triplet–singlet intersystem crossing (ISC). This "heavy atom effect" is well understood to arise from an increase in spin–orbit coupling (SOC).[4] We now report that effects from the presence of chlorine on olefinic bonds in molecules which are not constrained to planarity are far larger than those for classic spectroscopic examples. SOC calculations on vinyl chloride provide a satisfactory rationale for this unexpected observation.

Table I presents triplet state lifetimes, obtained by kinetic absorption spectroscopy in the presence of benzophenone, *p*-methoxyacetophenone, or thioxanthone as photosensitizers, by techniques we have previously used.[5,6] We have determined the lifetime of at least one nonchlorinated model for each chlorine-containing arylalkene, and we presume that geometric constraints when present are unaffected by the presence or absence of the chlorine. All chlorine-containing compounds could be recovered satisfactorily from prolonged preparative scale irradiation in the presence of the same photosensitizers, showing that C–Cl bond cleavage is not significant. Indene and 1,2-dihydronaphthalene underwent photodimerization, and in these two cases a modest extrapolation of measured lifetimes to low concentration was required.

The lifetimes of triplets containing the styrene chromophore without heavy atoms are long (microseconds) when the chromophore is held planar by ring constraints and short (20–100 ns) when the chromophore can approach the energetically preferred perpendicular structure,[6,7] consistent with the expected effects of the diminished T_1–S_0 gap and much-increased spin–orbit coupling in nonplanar configurations of the ethylenic moiety.[8] In the present work the chlorine is always in the β position of an arylethylene chromophore, and the variation in the restriction to planarity among the compounds in Table I allows an examination of the geometric dependence of enhancement of ISC due to heavy atom induced SOC.

Table I. Lifetimes of Arylalkene Triplets with and without Chlorine Substituents

triplet	lifetime,[a] ns	
	X = H	X = Cl
	1400	1300
	6800	14
	38 (38^b)	($<1.5^b$)
	(51^b)	($<1.5^b$)
	113	

[a] In heptane, room temperature, except as noted. Precision ±5%. [b] In benzene.

For the rigidly planar indene/2-chloroindene pair the effect of chlorine is clearly negligible. The somewhat more flexible but still near-planar pair 1,2-dihydronaphthalene/3-chloro-1,2-dihydronaphthalene can twist modestly toward the perpendicular minimum expected for the styrene chromophore. In this pair an enormous enhancement of ISC by chlorine results. For 2-chloro-1,1-diphenylpropene and 2,2-dichloro-1,1-diphenylethylene, the perpendicular minimum can be attained since there are no

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[1] The University of Texas at Dallas.

[2] Calspan Advanced Technology Center.

[3] Permanent Address: Cameron University, Lawton, OK.

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[7] Caldwell, R. A.; Cao, C. V. *J. Am. Chem. Soc.* **1981**, *103*, 3594–5.

[8] Caldwell, R. A.; Carlacci, L.; Doubleday, C. E. J.; Furlani, T. R.; King, H. F.; McIver, J. W. J. *J. Am. Chem. Soc.* **1988**, *110*, 6901–3.

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