Stereochemistry and Chiroptical Properties of the Nonplanar Nitrosamine Group in *N*-Nitrosoaziridines

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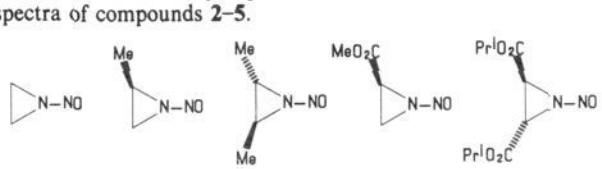
Abstract: The stereochemistry and the chiroptical properties of the nonplanar nitrosamine group were investigated by means of nonempirical quantum chemical calculations on 1-nitrosoaziridine (**1**), (2*R*)-2-methyl-1-nitrosoaziridine (**2**), and (2*S*,3*S*)-2,3-dimethyl-1-nitrosoaziridine (**3**), and by experimental measurement of the CD spectra of compounds **2**, **3**, (2*S*)-2-carbomethoxy-1-nitrosoaziridine (**4**), and (2*S*,3*S*)-2,3-bis(isopropoxycarbonyl)-1-nitrosoaziridine (**5**). The first electronic transition which occurs in the region 350–500 nm is assigned as $n_O \rightarrow \pi^*$, and is shown to be very similar to that found for *N*-acylaziridine and *gauche*-cyclopropyl ketones. For all three systems, the sign of the longest wavelength Cotton effect (CE) follows a "spiral rule" or, equivalently, a "reverse octant rule". The second transition which has an oppositely signed and stronger CE is assigned as a $\pi \rightarrow \pi^*$ transition of the inherently chiral NNO chromopore. The presence of the ester functionality (compounds **4** and **5**) results in a reversal of the CE signs of both the $n_O \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the nonplanar nitrosamine chromophore, that is, a reversal of the normal sector-related behavior of this chromophore.

Introduction

Earlier we investigated the stereochemistry and chiroptical properties of the nonplanar amide group in *N*-acylaziridines.[1] This group is characterized by a pyramidal configuration at the nitrogen atom, inherent chirality, and stereochemical lability. The same stereochemical properties may be expected for the nitrosamine group in *N*-nitrosoaziridines which are isoelectronic analogues of *N*-acylaziridines. This supposition is supported by semiempirical quantum chemical calculations[2] as well as, indirectly, by the UV,[3] NMR,[4] and photoelectron spectroscopic[5] data of *N*-nitrosoaziridines. However, except for the results of MNDO calculations,[2,4] there have been no detailed estimates of the dynamic stereochemistry, or even structural parameters. The instability of the compounds[3] imposes constraints on their experimental study. Therefore, investigation of *N*-nitrosoaziridines by means of high-level nonempirical quantum chemical calculations acquires added significance.

The chiroptical properties of the nonplanar nitrosamine group as found in *N*-nitrosoaziridines are of special interest. The nitrosamine chromophore has an electronic absorption band in the visible region of the spectrum, and another in the near-UV region, and has been widely used in CD spectroscopy.[6] However, only systems with an asymmetrically perturbed planar *N*-nitrosamine group have been studied to date. The effect of nonplanarity on the chiroptical properties is not known. The comparison with the nonplanar *N*-acyl chromophore, which in *N*-acylaziridines exhibits a bathochromic shift of the long-wavelength dichroic absorption band,[1] is of special interest. In *N*-acylaziridines, the sign of the Cotton effect (CE) of this band is determined by the intrinsic chirality of the chromophore.

In the present work,[7] we studied the stereochemistry and the chiroptical properties of the nonplanar nitrosamine group by means of nonempirical quantum chemical calculations on *N*-nitrosoaziridines, **1–3**, and by experimental measurement of the CD spectra of compounds **2–5**.

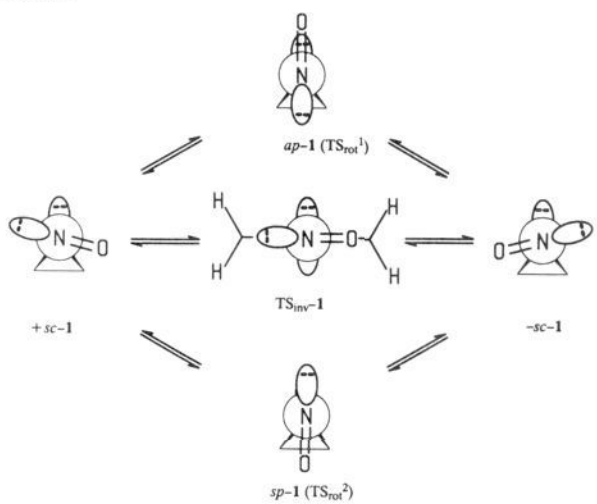


1 (2*R*) – 2 (2*S*, 3*S*) – 3 (2*S*) – 4 (2*S*, 3*S*) – 5

Results and Discussion

The structural parameters for all stable structures and a number of transition structures of *N*-nitrosoaziridines, **1–3**, are listed in Table I. The structures are defined in Schemes I and III. Calculated energies are listed in Table II. According to the

Scheme I



Scheme II

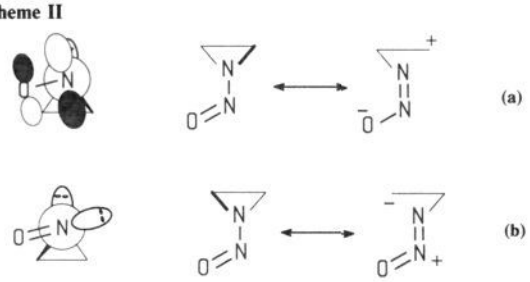


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Table I. Structural Parameters for *N*-Nitrosoaziridines **1–3** at the RHF 6-31G* Level

	structure[b]								anti / syn	
parameter[a]	*sc*-**1**	*ap*-**1**	*sp*-**1**	TS_{inv}-**1**	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**
NO	1.173	1.162	1.166	1.188	1.173	1.174	1.175	1.175	1.176	1.176
NN	1.369	1.414	1.420	1.300	1.365	1.365	1.359	1.357	1.358	1.356
NC_{anti}	1.436	1.467	1.469	1.395	1.439	1.437	1.440	1.433	1.442	1.434_5
NC_{syn}	1.434	1.467	1.469	1.398	1.436	1.436_5	1.435	1.442	1.437	1.445
CC_{ring}	1.489	1.456	1.457	1.527	1.490	1.490	1.491	1.492	1.493	1.494
$C_{Me}C_{anti}$					1.506	1.507			1.507	1.507
$C_{Me}C_{syn}$							1.511	1.511	1.511	1.511
$\angle_{CNC}$	62.5	59.5	59.4	66.3	62.4	62.5	62.5	62.5	62.5	62.5
$\angle NNC_{anti}$	118.3	108.8	115.4	146.1	118.6	118.4	120.5	120.1	120.6	120.5
$\angle NNC_{syn}$	120.9	108.8	115.4	147.6	120.9	121.5	122.1	124.1	122.5	124.2
$\angle NNO$	114.3	112.1	116.2	114.8	114.4	114.2	114.4	114.1	114.3	114.2
$\angle oop$[c]	54.6	68.2	60.4	0	54.5	54.2	52.6	51.4	52.2	51.2
$\angle ONNC_{anti}$	120.8			180.0	120.1	122.6	121.7	132.9	123.3	132.5
$\angle ONNC_{syn}$	54.6			0	46.8	49.2	47.0	57.4	48.4	56.9

[a] Bond lengths in Å, angles in deg. [b] See Schemes I and III. [c] The out-of-plane angle between the NN bond and the plane of the aziridine ring.

calculations, the stereochemistry of 1-nitrosoaziridine (**1**) has many features in common with the stereochemistry of 1-formylaziridine.[1] The poorer n-donor ability of the aziridine nitrogen results in a weakening of the amide-type $n_N-\pi_{NO}^*$ conjugation which is responsible for the planar geometry of more typical *N*-nitrosamines.[8] Nevertheless, the weakened $n_N-\pi_{NO}^*$ conjugation has a significant influence on the stereochemistry of nitrosoaziridine **1**. As in the case of *N*-acylaziridines, this manifests itself in the stabilization of a chiral synclinal rotamer, ±-*sc*-**1** (Scheme I, Table II). The NNO plane is not quite perpendicular to the direction of n_N, the lone pair of the ring nitrogen atom. Deviation from the orientation for maximum $n_N-\pi_{NO}^*$ overlapping[9] is probably due to an additional stabilizing interaction between one of the strained CN ring bonds and the π_{NO}^* orbital, as was found to be the case in 1-formylaziridine.[1] The lengthening of the aziridine *anti*-CN bond also is a result of this interaction. The *anti*-CN bond has a more favorable orientation for donation to the π_{NO}^* orbital (Scheme IIa). Unlike the case of 1-formylaziridine, however, in 1-nitrosoaziridine, the possibility also exists for back-donation from the nonbonding orbital of the nitroso nitrogen atom to the lowest empty orbital of the three-membered ring. This interaction should lead to the lengthening of the *syn*-CN bond (Scheme IIb). As a consequence, the difference in the CN bond lengths is not as great as was found in the case of 1-formylaziridine,[1] for which only the direct ring bond donation to the π^* orbital is available. As in the aziridine case also, the ring $\sigma_{CN}-\pi_{NO}^*$ interaction is substantially weaker than the $n_N-\pi_{NO}^*$ interaction since the achiral rotamers, *ap*-**1** and *sp*-**1** (Scheme I) are transition structures for rotation rather than minima. In these conformers, the n_N and π_{NO}^* orbitals are orthogonal and cannot interact, while the π_{NO}^* orbital is favorably disposed for donation from the Walsh-type σ bonding orbital of the ring. By contrast, the *ap* and *sp* rotamers of the carbocyclic analogue, nitrosocyclopropane, which lacks the competing $n_N-\pi_{NO}^*$ conjugation, are minima in the rotational potential curve.[10]

The difference in the energies of the *ap* and *sp* rotamers of nitrosoaziridine **1** (~3 kcal/mol, Table II) is almost the same as for the corresponding rotamers of 1-formylaziridine.[1] However, the relative stabilities are reversed. In **1**, the rotamer *ap*-**1** is more stable, perhaps as a consequence of the destabilizing eclipsing interaction of the nonbonded pairs in the *sp*-**1** rotamer.

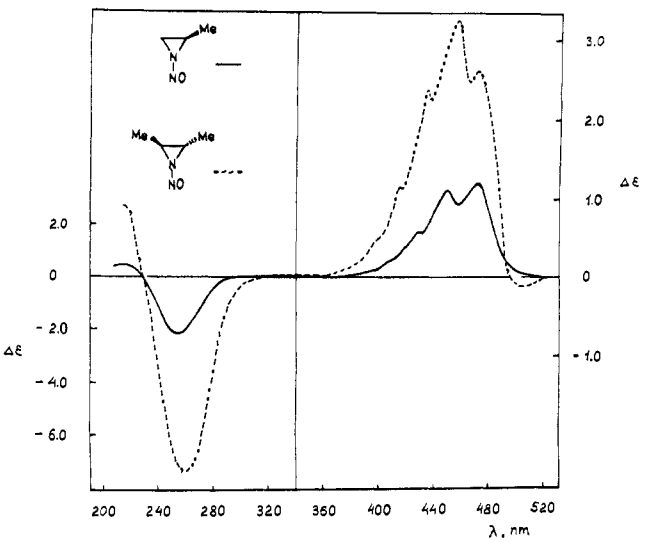

Figure 1. The CD spectra of *N*-nitrosoaziridines **2** and **3** in heptane at 10 °C.

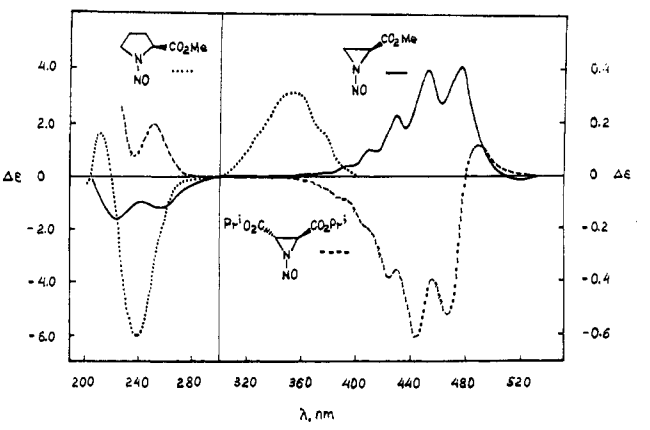

Figure 2. The CD spectra of *N*-nitrosoaziridines **4** and **5** and methyl (2*S*)-1-nitrosoproline in MeOH at 10 °C.

Weakening of the $n_N-\pi_{NO}^*$ conjugation due to the pyramidal distortion at the ring nitrogen atom significantly affects the barriers to rotation about the N–N bond, compared to typical unconstrained nitrosamines. The values found for **1** (3.6 kcal/mol and 6.9 kcal/mol) are substantially lower than the rotation barriers of *N*,*N*-dialkylnitrosamines (23–25 kcal/mol).[11] Nevertheless,

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(9) The dihedral angle between the NO bond and the bisector of the CNC angle must be 90° for maximal overlapping of the n_N and π_{NO}^* orbitals. This angle is equal to 84.3° in ±-*sc*-**1**.

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Table II. Calculated Energies of the Stationary Structures of *N*-Nitrosoaziridines **1–3**

structure[a]	*E*(RHF), au 6-31G*	E_{rel}, kcal/mol	*E*(RHF), au 6-31+G**//6-31G*	E(MP2), au 6-31+G**//6-31G*	E_{rel}, kcal/mol (incl ZPVE)
sc-**1**	−261.673 720	0.0	−261.687 932	−262.479 723	0.0
ap-**1**	−261.667 363	3.99	−261.682 263	−262.473 373	3.61
sp-**1**	−261.662 463	7.07	−261.675 979	−262.468 062	6.86
TS_{inv}-**1**	−261.657 263	10.33	−261.672 637	−262.466 298	8.08
2a	−300.714 925	0.0			
2b	−300.714 558	0.23			
2c	−300.712 484	1.53			
2d	−300.711 222	2.32			
3a	−339.753 176	0.0			
3b	−339.752 217	0.60			

[a] See Schemes I and III.

Table III. CD Spectra[a] of *N*-Nitrosoaziridines **2–5**

compound	solvent[c]	band I λ, nm (Δε[b])			band II λ, nm (Δε[b])	others λ, nm (Δε[b])
(2*R*)-**2**	H	472 (1.192)	450 (1.115)	429 (0.564)	253 (−2.20)	
		410 (0.206)	393 (0.062)			
(2*S*,3*S*)-**3**	H	506 (−0.121)	471 (2.667)	457 (3.303)	259 (−7.39)	
		435 (2.394)	414 (1.151)	397 (0.450)		
(2*S*)-**4**	H	480 (0.352)	454 (0.255)	430 (0.146)	261 (−0.85)	224 (−2.40)
		410 (0.055)	393 (0.018)			
	M	476 (0.415)	452 (0.399)	429 (0.230)	257 (−1.24)	224 (−1.67)
		409 (0.103)	393 (0.039)			
(2*S*,3*S*)-**5**	H	490 (0.133)	469 (−0.506)	444 (−0.552)	252 (1.21)	
		423 (−0.346)	404 (−0.170)	388 (−0.073)		
	M	489 (0.115)	467 (−0.527)	443 (−0.624)	252 (2.02)	
		423 (−0.394)	404 (−0.194)	389 (−0.085)		

[a] At 10 °C. [b] Approximate; the instability of the compounds precludes the determination of accurate Δε value (see text). [c] H = *n*-heptane, M = methanol.

Table IV. Calculated[a] Electronic Properties for *N*-Nitrosoaziridines **1–3**

property	+*sc*-**1**	**2a**	**2b**	**2c**	**2d**	**3a**	**3b**
IP,[b] eV							
1	10.29	9.81	9.77	9.77	9.64	9.71	9.59
2	10.70	10.30	10.28	10.13	10.17	9.88	9.96
3	13.10	12.23	12.35	12.34	12.35	12.03	11.95
μ, D	3.487	3.445	3.380	3.565	3.558	3.591	3.646
$S_0 \rightarrow S_1$							
E, eV	3.49	3.53	3.51	3.57	3.55	3.52	3.48
$[R]^r$	−16.2	20.9	−17.2	−19.5	21.6	32.5	−14.2
$([R]^v)$	−16.8	5.5	−2.3	−17.0	3.9	1.0	−20.6
f	0.0016	0.0025	0.0022	0.0032	0.0022	0.0028	0.0025
description	$n \rightarrow \pi^*$						
$S_0 \rightarrow S_2$							
E, eV	7.71	7.97	7.94	7.97	8.04	7.87	7.94
$[R]^r$	111.6	−118.2	108.2	105.1	−100.5	−121.1	54.0
$([R]^v)$	92.4	−75.7	77.2	83.8	−72.5	−80.5	48.6
f	0.0934	0.0518	0.0486	0.0431	0.0965	0.0550	0.1231
description	$\pi \rightarrow \pi^*$						
$S_0 \rightarrow S_3$							
E, eV	8.27	8.43	8.40	8.40	8.32	8.30	8.21
$[R]^r$	−52.8	74.3	−76.7	−52.8	52.8	69.3	−8.2
$([R]^v)$	−43.6	48.4	−49.6	−41.6	31.3	44.4	−6.9
f	0.0216	0.0709	0.0660	0.0612	0.0111	0.0592	0.0007
description	Rydberg, $n \rightarrow$ 3s, 3p						

[a] For +*sc*-**1**, the results were obtained with the 6-31+G* basis set; for **2** and **3**, the smaller 6-31G* basis set was used. [b] By the method of ref 17.

the n_N–π_{NO}^* conjugation is sufficient to lower the barrier to pyramidal inversion compared to unsubstituted aziridines.

The stereochemical lability of the nitrosamine group in *N*-nitrosoaziridines is confirmed indirectly by the NMR data,[4] according to which slow rotation or inversion were not observed in these compounds even at low temperatures. Thus, for an experimental study of the chiroptical properties of the intrinsically chiral nitrosamine group, it will be necessary to have present additional asymmetric centers which can induce a shift of the conformational equilibrium toward one of the *sc* rotamers. The substituted nitrosoaziridines **2–5** fulfil these requirements.

In the CD spectra of nitrosoaziridines **2–5**, two main absorption bands are observed, one in the region 390–500 nm (band I) and the other at 250–260 nm (band II). These are shown in Figures 1 and 2, and their characteristics are listed in Table III. Band I has vibronic structure as has also been observed for planar nitrosamines.[6] However, unlike in the case of planar nitrosamines, for example, methyl (2*S*)-1-nitrosoproline,[6b] substitution of heptane as solvent by a more polar, protic, solvent such as methanol, has practically no effect either on the vibronic structure or absorption position of band I in the CD spectra of nitrosoaziridines **4** and **5** (Table III, Figure 2). Evidently, the nonplanar nitrosamine group is substantially less polar than a planar nitrosamine group, another consequence of the reduced n_N–π_{NO}^* conjugation.

The difference in wavelengths of bands I and II (~180 nm) in the experimental CD spectra corresponds to an energy sepa-

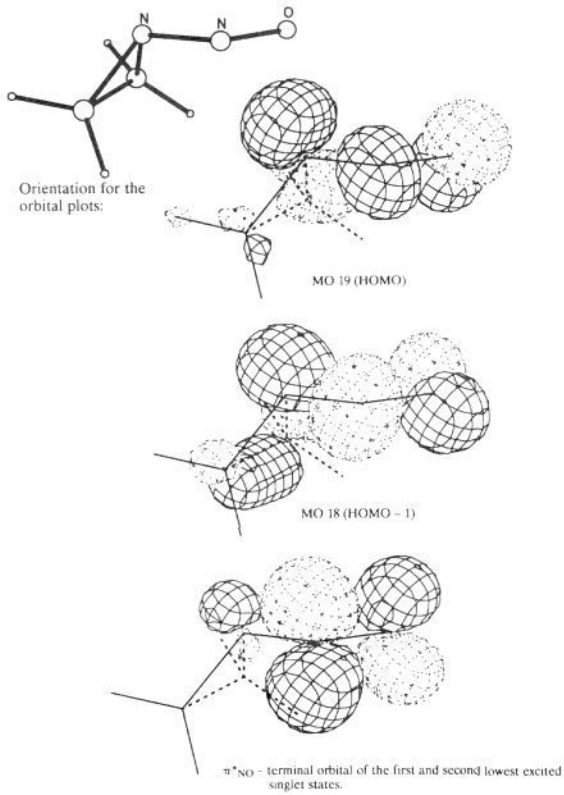


Figure 3. The two upper occupied molecular orbitals and the lower unoccupied MO involved in the electronic transitions of 1-nitrosoaziridine **1**:6-31G* basis set; contour 0.075.

ration of about 2 eV in the two lowest singlet states. The calculated energy differences for **1–3** (Table IV) are even larger since the computational method does not incorporate correlation corrections from doubly or more highly excited configurations. The orbital description of these states may be examined using nitrosamine **1** as a specific but typical case. Both states are valence states. In each case, the electronic excitation terminates in a π^* orbital (Figure 3) delocalized over the NNO fragment. In terms of canonical Hartree–Fock molecular orbitals (MO) in the configuration interaction (CI) expansion, the state descriptions are dominated by the same two configurations, MO19 $\rightarrow \pi^*$ and MO18 $\rightarrow \pi^*$. In the case of the first state, which corresponds to band I, the description includes 68% excitation from MO19 to the π^* orbital, and 28% excitation from MO18 to the same π^* orbital. The molecular orbitals MO19 and MO18 are the HOMO and HOMO − 1 orbitals shown in Figure 3. Similarly, the CI description of the second state, which corresponds to band II, is composed mainly of the same two configurations in different proportion, 26% and 59%, respectively, and phase.

Examination of MOs 19 and 18 (Figure 3) reveals that the orientations of the 2p orbitals on the N and O atoms of the nitroso group are neither in the plane of the NNO fragment, nor perpendicular to it. By contrast, the terminal π^* orbital is very close to perpendicular to the NNO plane. Mixing by CI of the contributions of the two orbitals in the two excited states may be approximately analyzed in terms of a single orbital (Figure 4) since the two major determinantal configurations differ only by one orbital (the π^* orbital being essentially the same in the two configurations). In effect, the CI mixing of MO18 and MO19 in the first state produces an originating orbital in which the 2p orbital on O and the *sp* hybrid orbital on N (of –NO) are more nearly in the NNO plane and the contribution from the ring is diminished. The originating orbital for the first state therefore closely resembles the nonbonded orbital, n_O, of a carbonyl group, and the transition to the first state may be described in the same terms, as a $n \rightarrow \pi^*$ transition. The low value for the computed oscillator strength, 0.0016, completes the analogy.

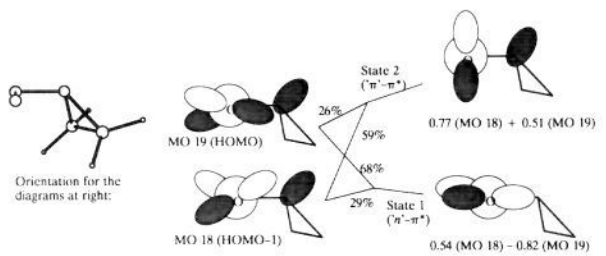


Figure 4. A description of the CI orbital mixing to produce the originating orbitals for the first two electronic transitions of 1-nitrosoaziridine **1**.

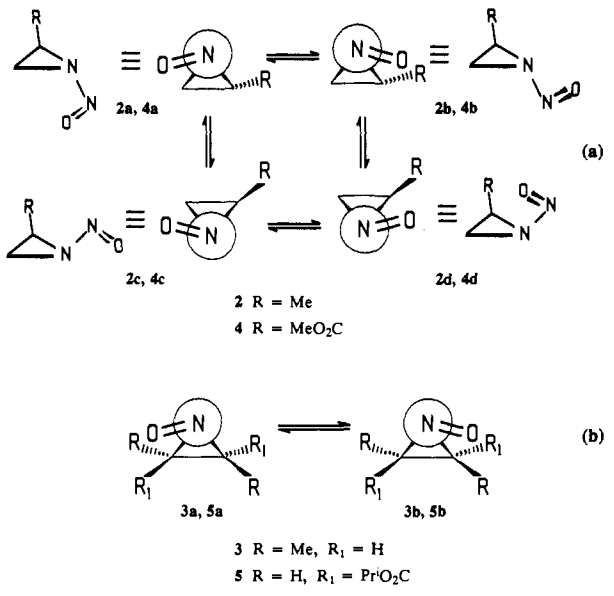
Configurational mixing for the second state also accomplishes a rotation of the 2p orbital of oxygen, producing an orbital which is very nearly perpendicular to the NNO plane. At the same time, the contribution from the central N atom is greatly diminished while the weight of the ring N is increased. In effect, the resulting orbital resembles the highest occupied MO of a four-electron three-orbital π system, such as that of the enolate anion or the amide group. The electronic transition to this state may therefore be described as $\pi \rightarrow \pi^*$. The higher calculated oscillator strength, 0.0934, is consistent with this interpretation.

Thus, the nonplanar nitrosamine chromophore in *N*-nitrosoaziridines has, qualitatively, the same orbital origin of the lowest two electronic states as the planar chromophore in more typical nitrosamines.[6b,c] However, in comparison with the latter, a noticeable bathochromic shift of both dichroic absorption bands is observed in the CD spectra of nitrosoaziridines **2–5**. For band I, this shift is about 100 nm, and is essentially independent of the nature of the carbon substituents. The difference in the positions of the dichroic absorption bands of planar methyl (2*S*)-1-nitrosoproline and nonplanar 1-nitrosoaziridine carboxylic esters, **4** and **5**, is readily observed in Figure 2. Indeed, the relative position of band I in the electronic absorption spectra of nitrosamines may serve as a measure of nonplanarity of the chromophore owing to the sensitivity. From the orbital origin of the first state, it follows that the bathochromic shift of band I of the nonplanar nitrosamine, as in the case of nonplanar amides,[1] is a consequence of lowering of the π_{NO}^* orbital energy owing to a weakening of the n_N–π_{NO}^* conjugation.

Nitrosamines **2–5** have short lifetimes and decompose partially during the course of the CD measurements, as a consequence of which the $\Delta\epsilon$ values recorded in Table III are only approximate. The products of the decomposition, nitrous oxide (N_2O) and olefins, are not optically active and do not affect the shape of the CD spectra. Repeated measurements of the spectra at different concentrations, at temperatures ≤10°, and using high scan rates, permit two qualitative conclusions: (a) in each case, the intensity of band I is lower than band II; (b) 2,3-disubstituted nitrosoaziridines, i.e., **3** and **5**, have more intense dichroic bands than 2-monosubstituted nitrosoaziridines, i.e., **2** and **4** (Table III, Figures 1 and 2), although the difference is less strongly expressed in the case of the carboxylic esters **4** and **5**.

Four conformational isomers, **2a–d** and **4a–d** (Scheme IIIa), can contribute to the observed Cotton effects (CE) of 2-monosubstituted nitrosoaziridines **2** and **4**. A simpler two-position equilibrium occurs in the case of 2,3-trans-disubstituted nitrosoaziridines **3** and **5** (Scheme IIIb). According to calculations on all isomers of methyl-substituted nitrosoaziridines **2** and **3** (Tables I and II), the sterically less hindered isomers, **2a** and **3a**, are preferred in each case. The difference in energies of invertomers **2a** and **2c**, 1.53 kcal/mol, is determined by the destabilizing steric interaction of the cis-eclipsed nitroso and methyl groups. This interaction is noticeably more important than the van der Waals repulsion between the O and H atoms of the syn-oriented nitroso and methyl groups, the only interaction contributing to the energy difference between rotamers **3a** and **3b**, both of which have cis-eclipsed NO and Me groups. The larger population of rotamer **2a** over **2b**, which is also sterically unencumbered, can be explained by the interaction between the nitroso group and the ring. As

Scheme III



discussed above (Scheme II), the presence of the methyl group at C_2 makes the C_2N bond a better donor and a poorer acceptor compared to the unsubstituted C_3N bond. The slight but consistent lengthening of the ring CN bond which has the anti orientation relative to the NO bond indicates the presence of the ring CN donor–π_{NO}^* acceptor interaction. Only in isomers **2d** and **3b**, where steric interaction between the nitroso group and the cis methyl group dominates, is the lengthening not seen.

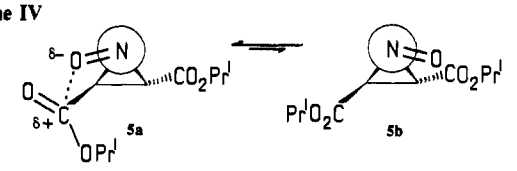
In spite of the diastereomeric relationship between the isomers **2a–d**, and between the isomers **3a** and **3b**, the CE signs of the first two transitions of each isomer are determined only by the intrinsic chirality of the nitrosamine group (Table IV). As in the case of homochiral nitrosoaziridine **1**, the *+sc* rotamers, **2b**, **2c**, and **3b**, have a negative sign of the first CE and a positive second CE. The *–sc* rotamers, **2a**, **2d**, and **3a**, have the reverse characteristics. All conformers of nitrosoaziridine **2** have similar rotational strength values of the first transition and also of the second, indicating that the methyl group is a weak perturber. The presence of the two methyl groups in nitrosoaziridine **3** induces larger differences in the rotational strengths of the two isomers **3a** and **3b** (Table IV).

Assuming $\Delta S° = 0$, one can estimate the equilibrium ratio of the isomers **2a**:**2b**:**2c**:**2d** as 0.57:0.38:0.04:0.01, and of the rotamers **3a**:**3b**, as 0.74:0.26, on the basis of the relative energies listed in Table II. From these ratios, the rotational strength of the equilibrium mixture of the isomers **2** is +4.8 ($\times 10^{-40}$ cgs) for the first transition and –23.1 for the second. For **3**, the corresponding results are +20.4 and –75.6. The CE signs are in complete agreement with the experimental observations (Table III, Figure 1). Moreover, qualitative agreement between calculated and experimental intensities is also observed: the first CE has a smaller intensity in comparison with the second; the rotational strengths of nitrosoaziridine **3** are higher than the rotational strengths of the monomethyl derivative, **2**.

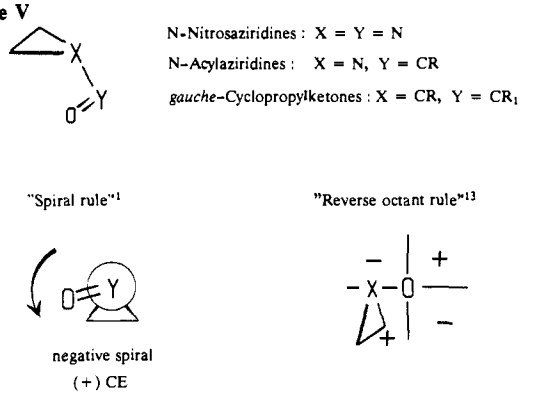
The calculated data offer an explanation for the presence of the weak negative CE at 506 nm in the CD spectrum of nitrosoaziridine **3** (Figure 1, Table III). This CE is probably due to rotamer **3b** which, according to the calculation, has a slightly longer wavelength band I with a negative sign.

The nitrosoaziridine carboxylic esters **4** and **5** present a more complicated situation because of the presence of the additional functionality, the ester group(s), and the consequent possibility of specific electrostatic interactions between the ester and nitroso groups. If, on the one hand, one were to assume that specific interactions are absent, then rotamer **5b** with the anti orientation of the nitroso and ester groups should be preferable for steric reasons (Scheme IIIb). It then follows that for nitrosamine **4**, isomer **4a** (Scheme IIIa) is the most populated as deduced from the signs of the observed CEs. However, donor–acceptor arguments advanced earlier (Scheme II) dictate that this isomer should *not* be preferred over isomer **4b** since the presence of the electronegative carboxy ester group would render the C_2N bond a poorer donor but a better acceptor than the unsubstituted C_3N bond, thereby favoring **4b**. On the other hand, the existence of attractive electrostatic interactions between cis-oriented NO and RO_2C groups are well documented in *N*-nitrosamino acids.[6b] If this kind of interaction can take place in nitrosoaziridine carboxylic ester **5** (Scheme IV), the rotamer **5a** may dominate and be responsible for the observed CE signs. A similar argument in the case of nitrosoaziridine **4** would require that the major isomer be **4b** which has the opposite orientation of the nitroso group and oppositely signed CEs in comparison with **5**. Such a shift of the conformational equilibrium toward **4b** would be consistent with the donor–acceptor views expressed in connection with Scheme II, given the expected effect of the carbalkoxy group as discussed above. The consequence of the second alternative is that the ester functionality results in a *reversal* of the CE signs of both the $n_O \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the nonplanar nitrosamine chromophore, in comparison with the *C*-methyl substituted *N*-nitrosoaziridines. Unfortunately, the molecules **4** and **5** are both too large for a direct verification of this effect by ab initio calculations at present. It is noted, however, that the anomalous effect of RO_2C groups on CE signs has been observed earlier in the case of *N*-haloaziridines[12] and also in the case *N*-acylaziridines[1] which have the electronically similar nonplanar amide chromophore.

Scheme IV



Scheme V



In summary, many common peculiarities between the nonplanar chromophores, the nitrosamine in *N*-nitrosoaziridines, and the amide moiety in *N*-acylaziridines have been found: the intrinsic chirality and stereochemical lability; the essential bathochromic shift of the long wavelength absorption band in comparison with the planar chromophore; very similar orbital origins for the first electronic transition; and the same relation of the first CE sign with the intrinsic chirality of the chromophore (Scheme V). Moreover, *gauche*-cyclopropyl ketones for which, previously, a "reverse octant rule" (Scheme V) had been proposed,[13] have the same orbital origin of the first CE and the same relationship of the CE sign with the stereochemistry of the molecule. In all three cases, the three-membered ring together with the gauche-oriented unsaturated group (C=O, N=O) form an intrinsically chiral chromophore, the long wavelength dichroic absorption band of which is due to the $n_O \rightarrow \pi^*$ transition. Therefore, a "reverse octant rule" or a "spiral rule" may be used interchangeably for

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N-acyl- and *N*-nitrosoaziridines, and for *gauche*-cyclopropyl ketones. Both approaches lead to the same result.

Methods

Theoretical. The geometries of 1-nitrosoaziridines **1–3** were fully optimized by Hartree–Fock SCF calculations at the 6-31G* level by using the GAUSSIAN 90 system of programs.[14] In the case of **1**, stationary points corresponding to transition structures for rotation about the N–NO 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).[15,16] For the purpose of determining the transition properties, the wave functions of **1** were redetermined using the internal 6-31+G* basis set, which includes additional diffuse s and p functions in the basis sets of the C, N, and O atoms. Addition of the diffuse functions permits a better description of the lowest few Rydberg states. The size of compounds **2** and **3** precludes use of the larger basis set. For these, transition properties were calculated using the 6-31G* basis set. Ionization potentials are calculated using a many-body perturbation theory correction to Koopmans' theorem based on the work of Pickup and Goscinski.[17] The frontier orbitals are displayed as modified Jorgensen–Salem plots.[18]

The method used to calculate oscillator and optical rotatory strengths is the same as was used previously[1,12,19,20] and has been described in detail elsewhere.[21] Partially correlated wave functions for the ground and excited states are determined to first order in Rayleigh–Schrödinger perturbation theory,

$$\Psi_n = \Psi_n^0 - \sum_j a_{nj}\Phi_j^0 \tag{1}$$

where

$$a_{nj} = \langle\Psi_n^0|H|\Phi_j^0\rangle/(\langle\Phi_j^0|H|\Phi_j^0\rangle - \langle\Psi_n^0|H|\Psi_n^0\rangle) \tag{2}$$

H is the exact Hamiltonian, Φ_j^0 is a singlet singly or more highly excited configuration derived from the Hartree–Fock determinant, Φ_{HF}, and Ψ_n^0 is a linear combination of strongly interacting Φ_l^0 ($l \neq j$) selected from at most singly excited configurations. Thus, for the ground state, $\Psi_0^0 = \Phi_{HF}$. All configurations for which the interaction coefficient a_{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 $\langle r\rangle_{0n}$ and velocity $\langle v\rangle_{0n}$ formalism and magnetic dipole transition moments $\langle m\rangle_{0n}$ are explicitly evaluated from

$$\langle r\rangle_{0n} = \langle\Psi_0|\mu|\Psi_n\rangle \tag{3}$$

$$\langle v\rangle_{0n} = \langle\Psi_0|\nabla|\Psi_n\rangle/(E_n - E_0) \tag{4}$$

$$\langle m\rangle_{n0} = -i\langle\Psi_n|\mathbf{m}|\Psi_0\rangle \tag{5}$$

where the dipole, gradient, and magnetic moment operators, μ, ∇, and $\mathbf{m}$, have their usual definitions and

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

Oscillator strengths f_{0n} are calculated by the "mixed" formalism

$$f_{0n} = \frac{2}{3}\langle\Psi_0|\nabla|\Psi_n\rangle\cdot\langle r\rangle_{n0} \tag{7}$$

Optical rotatory strengths are evaluated as

$$[R_{0n}]^r = \langle r\rangle_{0n}\cdot\langle m\rangle_{n0} \tag{8}$$

and in the origin independent form

$$[R_{0n}]^v = \langle v\rangle_{0n}\cdot\langle m\rangle_{n0} \tag{9}$$

The extent of the deviation of $\langle r\rangle$ and $\langle v\rangle$ from collinearity and in 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 ^{1}H NMR spectra were determined on a Bruker WM-400 (400.13 MHz) and a Varian XL-200 (200 MHz) spectrometer, from TMS. Optical rotation angles were measured on Autopol III (at 589 nm) and Polamat A (at 546 nm) polarimeters.

(2*R*)-2-Methylaziridine,[22] (2*S*)-2-methoxycarbonylaziridine,[23] and methyl (*S*)-1-nitrosoproline[6b] were prepared as previously described.

(2*S*,3*S*)-2,3-Dimethylaziridine and (2*S*,3*S*)-2,3-bis(isopropyloxycarbonyl)aziridine were obtained by reactions of the corresponding azido alcohols with Ph_3P.[24]

(2*S*,3*S*)-2,3-Dimethylaziridine: yield 71%, bp 74–75 °C, $[\alpha]^{20}_D$ −101.6° (*c* 1.7, heptane) (lit.[25]: bp 74.5–74.8 °C, $[\alpha]^{20}_D$ −103.8° (*c* 0.22, heptane)). ^{1}H NMR (200 MHz) spectrum in $CDCl_3$ δ, ppm (*J*, Hz): 0.16 broad s (NH), 1.18 d (Me_2, ^3J = 5.1), 1.64 m (2 H).

(2*S*,3*S*)-2,3-Bis(isopropyloxycarbonyl)aziridine: yield 68%, bp 91–92 (1 mm), $[\alpha]^{20}_{546}$ +137.6 (*c* 2.4, heptane). ^{1}H NMR (400 MHz) spectrum in toluene-d_8 δ, ppm (*J*, Hz): 0.90 d (Me, ^3J = 6.3), 0.92 d (Me, ^3J = 6.3), 0.96 d (Me_2, ^3J = 6.3), 1.60 broad m (NH), 2.7 dd (HC_{ring}, $^3J^{cis}_{CHNH}$ = 9.6, $^3J^{trans}$ = 2.3), 2.94 dd (HC_{ring}, $^3J^{trans}_{CHNH}$ = 8.5), 4.81 m, and 4.87 m ($HCMe_2$).

Nitrosation of Methyl-Substituted NH-Aziridines. A solution of ClNO (0.0327 g, 0.5 mmol) in absolute heptane (1 mL) was added to the NH-aziridine (1 mmol) in absolute heptane (4 mL) with cooling (−78 °C) and stirring. After 15 min at −40 to −30 °C, the precipitate was filtered off under reduced pressure of dry argon at the same temperature. The resulting solution was kept at −78 °C and was used for preparation of solutions for the CD measurements in thermostatic cells (1 cm for band I and 0.1 cm for band II) at 3–10 °C, scan speed 50–100 nm/min.

Nitrosation of NH-aziridinecarboxylic esters was carried out by the same procedure, with equimolar quantities of the substrate, Et_3N and ClNO in absolute ether.

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