Chiroptical Properties of the Non-planar Nitrosamine Chromophore in *N*-Nitrosaziridines

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The sign of the long-wavelength Cotton effect in the circular dichroism (CD) spectra of *N*-nitrosaziridines, possessing a non-planar nitrosamine chromophore, is determined by the intrinsic chirality of the chromophore, as in the cases of *N*-acylaziridines and *gauche*-cyclopropylketones.

The nitrosamine chromophore has electronic absorption bands in the near (340–360 nm) and mid (∼230 nm) ultraviolet regions, and is widely used in CD spectroscopy.[1] Hitherto, only chiral compounds with a planar nitrosamine group have been studied. Unlike the normal *N*,*N*-dialkylnitrosamines, *N*-nitrosaziridines possess a non-planar, intrinsically chiral, nitrosamine group, owing to the pyramidal configuration at the aziridine nitrogen and a preference for a *gauche* (synclinal) conformation around the NN bond.[2]

We have measured, for the first time, the CD spectra of optically active nitrosaziridines **1**, **2**[†] (Fig. 1) and have calculated the optical rotational strengths of transitions to the lowest electronic singlet states of all isomers of the compounds, *i.e.* **1a–d**, and **2a,b** (Scheme 1, Table 1).

Two main absorption bands are observed in the CD spectra of nitrosaziridines **1**,**2**, band I in the region 390–500 nm, and band II at about 250 nm (Fig. 1). Band I exhibits vibronic structure as has also been observed for planar nitrosamines.[1] The difference in wavelength between bands I and II (∼180 nm) is closely reproduced by the calculations of the two lowest electronic singlet states (190–200 nm, Table 1). Both states are valence states and have the same orbital origin as in the case of the planar nitrosamine chromophore.[1] The transition to the first state may be described as $n_O \rightarrow \pi_{NO}^*$, where the n_O orbital lies in the plane of the NNO fragment and is the 2p orbital on oxygen with an out-of-phase admixture of the 'sp2' hybrid orbital on the nitrogen of the nitroso group. The second transition is to the π_{NO}^* orbital also, but originates from a π orbital very nearly perpendicular to the NNO plane, and resembles the highest occupied molecular orbital of a

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[†] Nitrosaziridines **1**, **2** were obtained in n-heptane solutions by the action of 0.5 equiv. ClNO on (2*R*)-2-methylaziridine[3] and on (2*S*, 3*S*)-2,3-dimethylaziridine,[4] respectively, at −70 °C, as previously described for the racemic compounds.[5] Compounds **1**, **2** partially decompose during the CD measurements. Consequently the $\Delta\varepsilon$ values in Fig. 1 are not accurate. However, the qualitative features of the CD spectra were reproduced in several experiments.

Table 1 Calculated energies[a] and electronic properties[b] for *N*-nitrosaziridines, **1** and **2**

		1a	**1b**	**1c**	**1d**	**2a**	**2b**
Relative energy[c] /kJ mol^{-1}		0	0.96	6.41	9.71	0	2.51
$S_0 \rightarrow S_1$	ΔE/eV	3.53	3.51	3.57	3.55	3.52	3.48
(n $\rightarrow \pi^*$)	[R][d]	20.9	−17.2	−19.5	21.6	32.5	−14.2
	f[e]	0.0025	0.0022	0.0032	0.0022	0.0028	0.0025
$S_0 \rightarrow S_2$	ΔE/ev	7.97	7.94	7.97	8.04	7.87	7.94
($\pi \rightarrow \pi^*$)	[R][d]	−118.2	108.2	105.1	−100.5	−121.1	54.0
	f[e]	0.0518	0.0486	0.0431	0.0965	0.0550	0.1231

[a] RHF/6-31G* at 6-31G* optimized geometries. [b] Using the 6-31G* basis set and the perturbed CI procedure described previously.[6] [c] E(RHF): **1a** -300.714925 Hartree; **2a** -339.753176 Hartree. [d] 10^{40} cgs. [e] Oscillator strength.

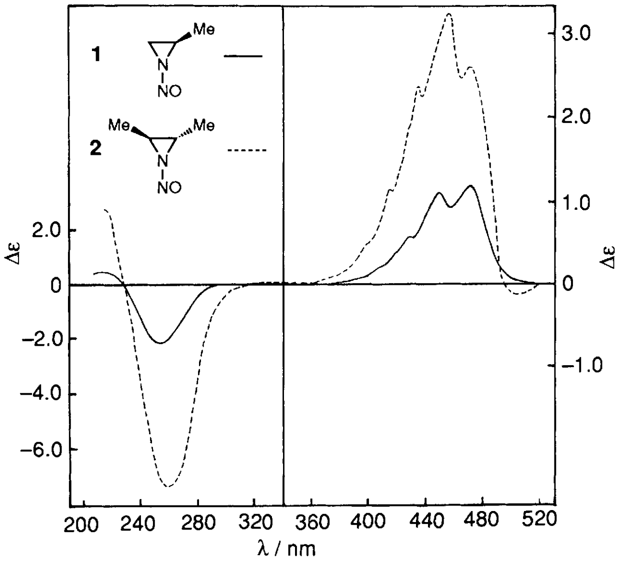
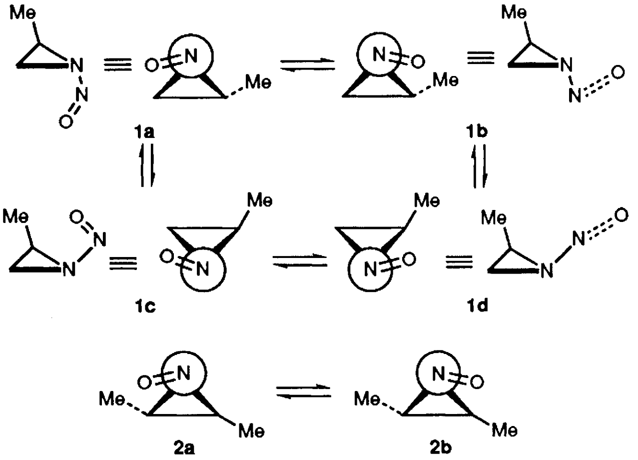


Fig. 1 The CD spectra of *N*-nitrosaziridines **1** and **2** in n-heptane at 10 °C

four-electron three-orbital π system, such as, for example, the amide group.[6] The calculated oscillator strengths (Table 1) are consistent with this interpretation. In the CD spectra of nitrosaziridines **1**, **2**, bands I and II, especially band I, show a significant bathochromic shift (~100 nm for band I) in comparison with other nitrosamines.[1] This shift is mainly due to a lowering of the π_{NO}^* orbital energy owing to weakening of the amide-like n_N–π_{NO}^* conjugation.

In spite of diastereoisomeric relations between isomers **1a–d**, and **2a**,**b** (Scheme 1), the Cotton effect (CE) signs of the first two transitions of each isomer depend only on the intrinsic chirality of the chromophore (Table 1). The (−)-synclinal rotamers, **1a**,**d**, **2a**, have a positive sign of the first CE and a negative sign of the second, and the (+)-synclinal rotamers, **1b**,**c**, **2b**, have the opposite CE signs.

Assuming $\Delta S^0 = 0$, the equilibrium ratio of isomers **1a** : **1b** : **1c** : **1d** may be estimated from the relative energies (Table 1) to be 0.57 : 0.38 : 0.04 : 0.01, and of rotamers **2a** : **2b** as 0.74 : 0.26. From these ratios and calculated value of rotational strengths, the optical rotatory strength of the equilibrium mixture of the isomers of nitrosaziridine **1** may be estimated to be +4.8 for the first transition and −23.1 for the second, in cgs units ($\times 10^{40}$). The corresponding values for **2** are + 20.4 and −75.6, respectively. These CE signs coincide with the experimental observations (Fig. 1). In addition, the relative intensities of the two bands are in qualitative agreement, *i.e.*, the first CE has a smaller intensity than the second for each compound, and the CE intensities of both transitions in the CD spectrum of nitrosaziridine **2** are higher than the corresponding intensities of nitrosamine **1**.



Scheme 1

Thus, the chiroptical properties of N-nitrosaziridines are rather closer to their topological and electronic analogues, *N*-acylaziridines[6] and *gauche*-cyclopropylketones,[7] than to the more usual *N*,*N*-dialkylnitrosamines with a planar nitrosamine chromophore. The three-membered ring, together with the *gauche* unsaturated group (C=O, N=O) forms an intrinsically chiral chromophore which has the same n-π* orbital origin of the long-wavelength CE, and the same relation of the sign of this CE with the stereochemistry of the chromophore in all three systems.

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