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Chiroptical Properties of the Inherently Non-planar Nitroamine Chromophore in *N*-nitroaziridines

Gennadii V. Shustov[a] **and Arvi Rauk***[b]

[a] *Institute of Chemical Physics, Russian Academy of Sciences, Moscow 117977, Russia*
[b] *Department of Chemistry, University of Calgary, Calgary, Alberta, Canada, T2N 1N4*

The long-wavelength Cotton effect (CE) of the nitroamine chromophore is very sensitive to structural non-planarity and helicity; the sign of this CE for *N*-nitroaziridines has the same connection with the intrinsic chirality of the chromophore as in the case of *N*-acyl-, *N*-nitroso-aziridines and aziridinones.

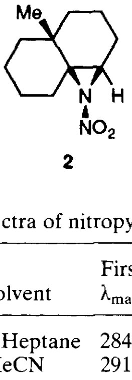
Nitroamines are characterized by electronic absorption in the accessible UV region near 280 nm and 240 nm and are considered as prospective chromophoric derivatives of chiral amines for the purpose of stereochemical investigations by means of circular dichroism (CD) spectroscopy.[1] Assuming a planar geometry for the nitroamine chromophore, the following chiral rules were offered: an octant rule[2] for the first CE near 280 nm and a quadrant rule[3] for the second one at 240 nm. In spite of confirmation by semiempirical quantum chemical calculations,[4] it was found[3] that the octant rule[2] does not work for 2-alkyl substituted nitropiperidines. The first CE sign in the CD spectra of the simple C_2-symmetrical nitropyrrolidine **1**† (Table 1), which is synthesized by us, also does not obey the octant rule.[2] We have supposed that the observed discrepancy can be caused by deviation of the nitroamine chromophore from its planarity by pyramidalization of the amine nitrogen and/or by twisting about the bond to the nitro group. Indeed, structural studies of some nitroamines[7] and, specifically, of nitropyrrolidine[8] confirm the pyramidal configuration of the amine nitrogen. According to the data of X-ray analysis[9] and non-empirical calculations,[10] such a chromophore is contained in *N*-nitroaziridines.

We have measured, for the first time, the CD spectra of optically active nitroaziridine **2**‡ (Table 1) and have calculated the optical rotational strengths of transitions to the lowest electronic singlet states of model nitroaziridines **3**, **4** (Table 2).

The CE, which is observed near 240 nm in the CD spectra of nitroaziridine **2** (Table 1), has parameters (λ_{max} and intensity) which are close to the parameters of the second CE (at 240 nm) of nitropyrrolidine **1** and other nitroamines,[3] whereas the first CE (at 300 nm) of nitroaziridine **2** differs in that it is bathochromically shifted and has considerable intensity.

According to the calculations (Table 2), these CEs of the nitroaziridine chromophore are caused by electronic transitions to the $\pi_{NO_2}{}^*$ orbital with maximum amplitude on the nitrogen atom. The initial orbitals are the following combina-

1



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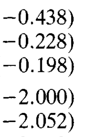

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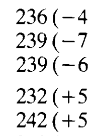
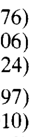


cis-**4**



trans-**4**

Table 1 CD spectra of nitropyrrolidine **1** and nitroaziridine **2**

Compound	Solvent	First CE λ_{max}/nm ($\Delta\varepsilon$)	Second CE λ_{max}/nm ($\Delta\varepsilon$)
1	*n*-Heptane	284 (−0.438)	236 (−4.176)
	MeCN	291 (−0.228)	239 (−7.506)
	MeOH	290 (−0.198)	239 (−6.124)
2	*n*-Heptane	298 (−2.000)	232 (+5.697)
	MeCN	300 (−2.052)	242 (+5.010)
	MeOH	299 (−2.349)	239 (+4.880)

Table 2 Calculated energies[a] and electronic properties[b] for model nitroaziridines, **3** and **4**

		3	**3a**[c]	*cis*-**4**	*trans*-**4**
Relative energy[d]/kJ mol^{-1}		0	2.2	7.1	0
α^e/°		56.4	71.4	68.1	54.8
β^e/°		56.4	41.4	44.1	57.8
$S_0 \rightarrow S_1$	ΔE/eV	5.89	5.87	5.93	5.93
($n_O{}^- - \pi_{NO_2}{}^*$)	[R]^f	0	−5.3	−5.9	+0.2
	f^g	0.0000	0.0001	0.0002	0.0000
$S_0 \rightarrow S_2$	ΔE/eV	6.63	6.62	6.69	6.66
($n_O{}^+ - \pi_{NO_2}{}^*$)	[R]^f	0	+2.9	+5.7	+3.3
	f^g	0.0038	0.0035	0.0038	0.0040

[a] RHF/6-31G* at 6-31G* optimized geometries. [b] Using the 6-31G* basis set and the perturbed CI procedure described previously.[13,14] [c] Obtained from **3** by 15° twist around the NN bond. [d] E(RHF): **3** −336.490248 Hartree; *trans*-**4** −375.532015 Hartree. [e] See Scheme 1. [f] 10^{40} cgs. [g] oscillator strength.

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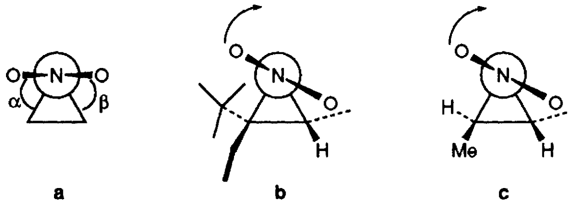
† (2*R*,5*R*)-1-Nitro-2,5-dimethylpyrrolidine **1**, m.p. 57–58 °C, $[\alpha]_D^{20}$ −165.7 (*c* 1.1, $CHCl_3$) was obtained from (2*R*,5*R*)-(−)-2,5-dimethylpyrrolidine[5] using the procedures of ref. 6.

‡ (1*R*,9*R*,10*R*)-10-Methyl-1,9-(*N*-nitroaziridino)decalin **2**, m.p. 38–42 °C, $[\alpha]_D^{20}$ −30.1 (*c* 1.4, *n*-heptane) was prepared from (*R*)-(−)-10-methyl-$\Delta^{1,8a}$-octalin-2-one {(*R*]-(−)-6-methylbicyclo[4.4.0]dec-1-en-3-one}[11] following the procedures which were described[12] for racemic **2**. The compounds **1**, **2** show satisfactory analytical and spectral data.



Scheme 1

tions of the n_O orbitals which lie nearly in the plane of the nitro group: the 'out-of-phase' combination (n_O^-) for the first transition; the 'in-phase' combination (n_O^+) for the second one. The non-bonding orbital of the aziridine nitrogen does not contribute to the initial n_O^- orbital. Therefore the bathochromic shift of the first CE of nitroaziridine **2** is due almost entirely to decreasing of the terminal $\pi_{NO_2}{}^*$ orbital energy, a consequence of weakening of the amide-like n_N-$\pi_{NO_2}{}^*$ conjugation.

The comparatively high intensity of the first CE of nitroaziridine **2** can be explained by the intrinsic chirality of the chromophore. The parent nitroaziridine, **3**, has a non-planar but symmetrical equilibrium conformation around the NN bond (C_s symmetry, Scheme 1 **a**, $\alpha = \beta$) resulting in zero values of the optical rotational strengths (Table 2). However, it is evident that in the case of nitroaziridine **2**, the steric interaction of the nitro group with the *cis*-oriented C-substitutent of the aziridine ring must lead to a deviation (Scheme 1 **b**) from the locally symmetrical conformation. Indeed the fully optimized structure of *cis*-nitroaziridine **4**, in which the same local environment of the chromophore is modelled, has the twisted right-spiral conformation of the nitro group (Scheme 1 **c**). By contrast, the *trans*-oriented C-substituent exerts a weak influence on the conformation around the NN bond: for *trans*-nitroaziridine **4** this conformation is close to the symmetrical one of the unsubstituted compound **3** (Table 2). The calculated optical rotational strength signs of the first two transitions of *cis*-**4** with the right-spiral conformation of the chromophore (Table 2) coincide with the experimental signs of nitroaziridine **2** (Table 1). The same signs of the rotational strengths are observed for the parent nitroaziridine **3a** in which a right-spiral deviation from its symmetrical equilibrium geometry has been artificially imposed (Table 2). The small left-spiral deviation which is calculated for *trans*-**4** is consistent with the small positive rotational strength calculated for the first transition.

Thus, the first CE sign of the inherently non-planar nitroamine chromophore is determined by the intrinsic chirality of the chromophore. As in the cases of the non-planar amide chromophore[13] in *N*-acylaziridines and aziridinones and of the non-planar nitrosoamine one[14] in *N*-nitrosoaziridines, the nitroamine chromophore with the right-spiral chirality is characterized by the negative first CE. It should be noted that the negative first CE is observed in the CD spectra of nitropyrrolidine **1** (Table 1) which can be assumed to possess the same right-spiral deformation of the chromophore due to local steric interactions.

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