N-Nitro-Substituted Azetidines and Aziridines. The Inherently Nonplanar Nitroamines: Conformational and Chiroptical Properties

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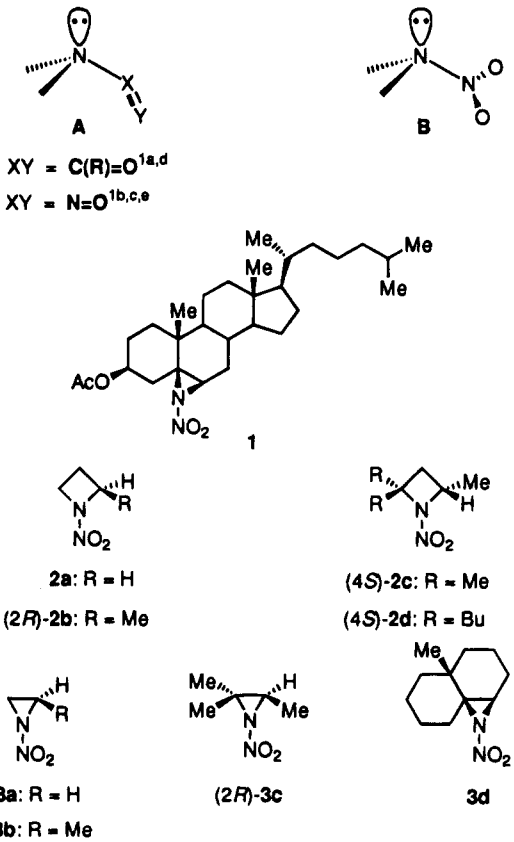
Optically active inherently nonplanar nitroamines, i.e., (2*R*)-1-nitro-2-methylazetidine (**2b**), (4*S*)-1-nitro-2,2-dibutyl-4-methylazetidine (**2d**), and (1*R*,9*R*,10*R*)-10-methyl-1,9-(*N*-nitroaziridino)decalin (**3d**), are synthesized and their CD, UV, and NMR spectra are studied. Experimental data are interpreted on the basis of nonempirical quantum chemical calculations of model compounds—the parent *N*-nitro-substituted azetidine **2a** and aziridine **3a** and their mono- and trimethyl derivatives **2a,b** and **3b,c**. It is shown that owing to the stereochemical lability of the pyramidal nitroamine chromophore, the closest asymmetrical environment causes torsional deformation of the chromophore and thus induces its intrinsic chirality. The latter determines the Cotton effect sign of the $n_O^- - \pi^*$ transition in accordance with a spiral rule, which was formulated for the non-planar amide and nitrosoamine chromophores. The wavelength of the Cotton effect depends mainly on the pyramidality of the ring nitrogen atom and the intensity on the amount of twisting around the NN bond.

Introduction

The present work is a continuation of our studies of chiroptical and conformational properties of nitrogen heterocycles containing nonplanar chromophores of type **A**.[1] The Cotton effect (CE) sign of the $n-\pi^*$ transition in CD spectra of these compounds is determined by the intrinsic chirality of the chromophore which in turn is induced by stereoelectronic interactions with the available chiral centers of the molecule owing to a conformational lability of the chromophore. Thus, it is possible to connect the CE sign of a chromophore of type **A** with the absolute stereochemistry of the molecule. If the amino nitrogen atom of a nitroamino group (**B**) is included into a strained four- or three-membered ring, the group can be assigned to type **A** chromophores since *N*-nitro-substituted azetidines and aziridines possess the pyramidal configuration of the ring nitrogen according to the data of X-ray analysis[2] and nonempirical quantum chemical calculations.[3] However, chiroptical properties of these inherently nonplanar nitroamines have not been studied. Moreover, as far as we know,[2a,4] hitherto, optically active *N*-nitroazetidines were not synthesized and any data on the optical activity of steroid *N*-nitroaziridine **1**[2a,5] are absent. Previous theoretical stereochemical investigations of *N*-nitro-substituted azetidines and aziridines were carried out on the parent compounds **2a** and **3a**, for which only the ground states and barriers of the rotation about the NN bond were calculated.[3]



We have carried out investigations of *N*-nitroazetidines **2a-d** and aziridines **3a-c**.[6] Derivatives **2b,d** and **3d** have

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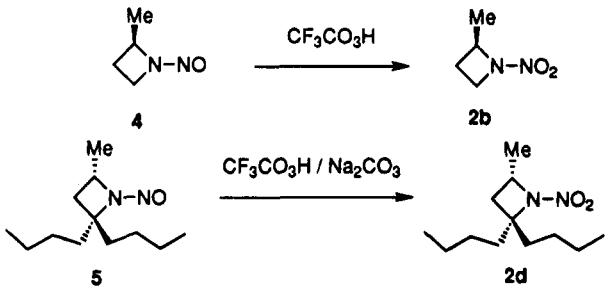
Scheme 1



been studied experimentally by means of CD, UV, and NMR spectra. For simple compounds **2a,b** and **3a**, nonempirical quantum chemical calculations of the stationary structures and lower excited states have been performed. In the cases of the highly substituted *N*-nitroazetidine **2d** and aziridine **3d**, simpler models **2c** and **3b,c**, having a similar closest stereochemical environment of the chromophore, were calculated. Usually such an approach proves its value.[1] In particular, it was recently shown for *N*-nitrosoazetidines[1e] that the rotational isomerism of long-chained 2-alkyl substituents does not exert a significant influence on the local geometry of the nitrosoamine chromophore and the chiroptical properties connected with its lower excited states.

Results and Discussion

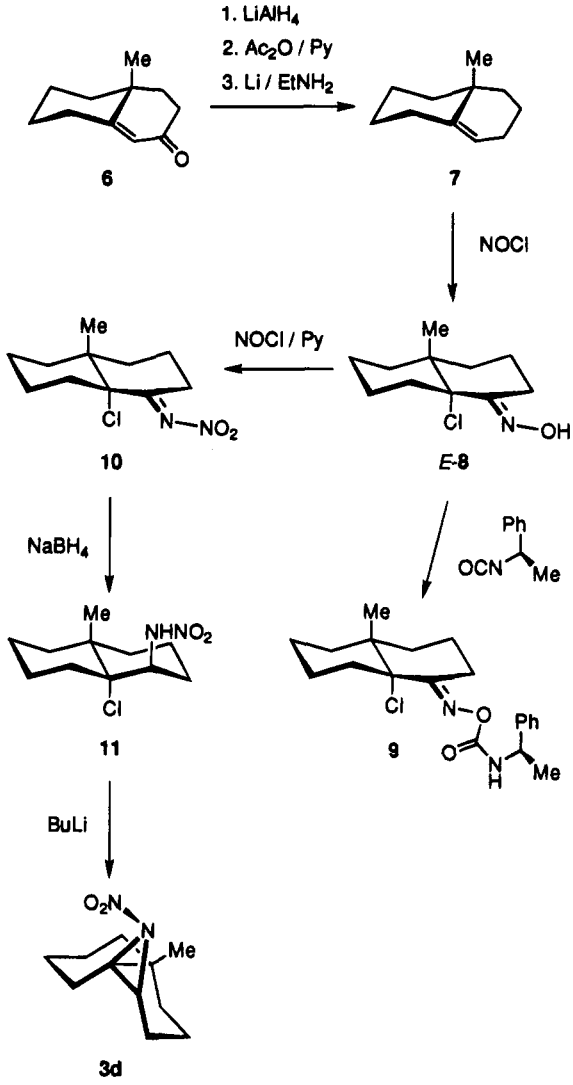
Synthesis. *N*-Nitroazetidines **2b,d** were obtained by oxidation[7a] of corresponding optically active *N*-nitroso derivatives **4** and **5** (Scheme 1).[1e] The yield of 2,2-dibutyl-substituted *N*-nitroazetidine **2d** is considerably increased when oxidation is carried out in the presence of sodium carbonate as a buffer.[7b] A decrease of reaction medium acidity is apparently important for suppression of acid-catalyzed reactions of an azetidine ring opening, which can be realized owing to the presence of the quaternary C(2) atom.

Optically active *N*-nitroaziridine **3d** was synthesized from (*R*)-10-methyl-$\Delta^{1,9}$-octalin (**7**) according to Scheme 2 described earlier[5] for racemic **3d**. In its turn, olefin **7** was prepared from (*R*)-10-methyl-1(9)-octal-2-one (**6**)[8a] (ee 76%) *via* the procedures of Marshall and Hochstetler.[8b]

It is known that nitrosohalogenation of $\Delta^{1,9}$-octalin **7**[5] and other similar olefins[9] is stereoselective: the halogen atom and vicinal methyl group have *trans*-diaxial orientation in reaction products.

A considerable deshielding of the equatorial proton at C(2) of oxime **8** indicates a *syn*-orientation (*E*-configuration) of the hydroxyimino group with respect to the α-methylene group.[10] Indeed, the chemical shift (3.27 ppm) of this proton is close to the shift (3.18 ppm) of the equatorial proton at C(6) of (*E*)-2-chloro-3-methylcyclohexanone oxime and is different from the value (2.25 ppm) which was found for the *Z*-isomer of the latter.[10b] According to a chiral rule[11] for cyclic six-membered α-hetero-substituted ketoximes, the negative sign of the CE at 215 nm ($\Delta\epsilon = -5.94$) in the CD spectrum of oxime

Scheme 2



8 in acetonitrile is in agreement with the geometry of this compound as (*E*)-9,10-*trans*-isomer (Scheme 2).

The enantiomeric excess of oxime (*E*)-**8**, *ca.* 76%, has been determined from the ^1H NMR spectrum of a mixture of the diastereomers of *O*-(*N*-(α-methylbenzyl))carbamoyl derivative **9** by integration of signals of the methyl group at C(10).

As in the cases of oxime (*E*)-**8** and nitrimine **10**, admixtures of diastereomers were not observed in the NMR spectra of nitroamine **11** and nitroaziridine **3d**. The values of the vicinal spin coupling constants ($^3J_{ea} = 5.3$ Hz, $^3J_{ee} < 1$ Hz) of the proton at C(1) with the protons at C(2), measured under conditions of the fast exchange of the proton of the nitroamino group of **11**, indicate the equatorial position of the proton at C(1) and, correspondingly, the axial *trans*-position of the nitroamino group with respect to the chlorine atom in this compound. Cyclization of nitroamine **11** with such configurations of the C(1), C(9), and C(10) atoms affords nitroaziridine **3d** with the *cis*-orientation of the aziridine ring and the methyl group at C(10). According to the X-ray data,[2] the steroid aziridine **1**, obtained *via* the analogous scheme,[5] has the same stereochemistry of the closest environment of the aziridine ring.

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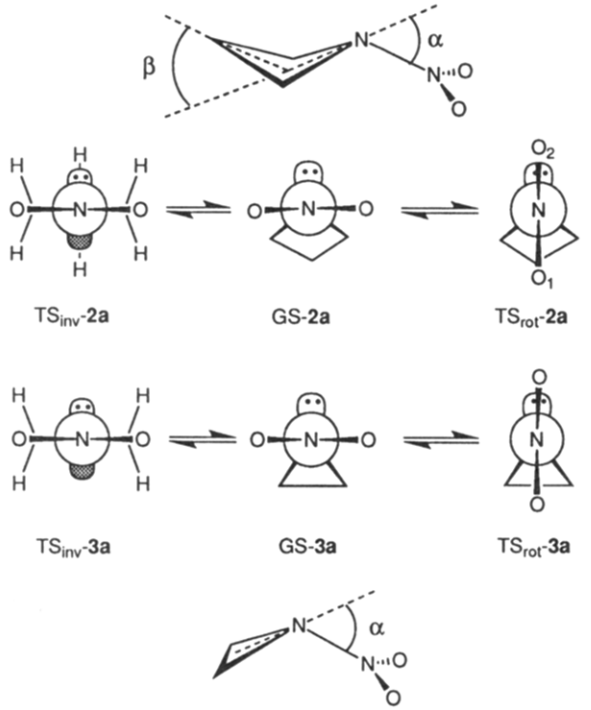
Table 1. Selected Geometrical Parameters[a] and Relative Energies[b] of the Stationary Structures of *N*-Nitroazetidines 2a–c and *N*-Nitroaziridines 3a–c at the RHF 6-31G* Level

	GS-**2a**	TS_{inv}-**2a**	TS_{rot}-**2a**	*cis*-**2b**	*trans*-**2b**	*trans*-**2c**	GS-**3a**	TS_{inv}-**3a**	*cis*-**3b**	*trans*-**3b**	*cis*-**3c**	*trans*-**3c**
N–O_1[c]	1.195	1.200	1.194	1.197	1.196	1.197	1.189	1.196	1.191	1.190	1.192	1.190
N–O_2[c]	1.195	1.200	1.181	1.196	1.194	1.197	1.189	1.196	1.190	1.189	1.192	1.192
N–N	1.343	1.311	1.415	1.336	1.344	1.338	1.382	1.313	1.378	1.380	1.368	1.375
N–CR_2[d]	1.464	1.446	1.480	1.457	1.463	1.486	1.442	1.391	1.441	1.444	1.457	1.461
N–CHMe				1.474	1.473	1.466			1.455	1.446	1.452	1.444
ONO	126.4	126.4	125.9	126.1	126.2	127.7	126.6	126.7	126.3	126.5	125.9	126.1
NNO_1[c]	116.8	116.8	118.2	117.1	116.9	117.2	116.6	116.6	116.0	116.5	116.8	116.2
NNO_2[c]	116.8	116.8	115.9	116.8	116.9	117.1	116.6	116.6	117.5	116.9	117.1	117.5
CNC	94.2	98.2	90.5	95.1	94.2	95.0	61.8	66.9	61.2	61.8	61.8	61.9
α[e]	39.3	0.0	52.2	32.2	39.8	34.5	57.9	0.0	56.3	57.6	52.6	55.2
β[e]	19.7	0.0	28.8	18.8	19.8	19.8						
$CNNO_1$[f]	31.3	0.0	51.9	−32.2	31.7	34.1	56.4	0.0	−68.1	57.8	56.5	−67.1
$CNNO_2$[f]	31.3	0.0	128.1	22.6	−31.4	−22.1	56.4	0.0	44.1	-54.1	−53.9	44.1
γ[f]	0.0	0.0	90.0	4.8	0.15	5.6	0.0	0.0	12.0	1.8	1.3	11.5
E_{rel}	0.0	2.5	12.7	2.2	0.0		0.0	16.4	1.7	0.0	2.9	0.0

[a] Bond lengths in Å, angles in deg. [b] In kcal/mol. [c] See Scheme 3 and Chart 1. [d] R = H for **2a,b** and **3a,b**; R = Me for **2c** and **3c**. [e] See Scheme 3. [f] See Chart 1.

Scheme 3



Conformational Analysis. As it was theorized, all calculated compounds **2a–c, 3a–c** in their ground states are characterized by a pyramidal configuration of the ring nitrogen atom and by the conformation around the NN bond with a maximum possible overlapping of the n_N and $\pi^*_{NO_2}$ orbitals. The rotamers with the orthogonal orientation of these orbitals are the rotation transition states (TS_{rot}-**2a** and **3a,** Scheme 3, Table 1).

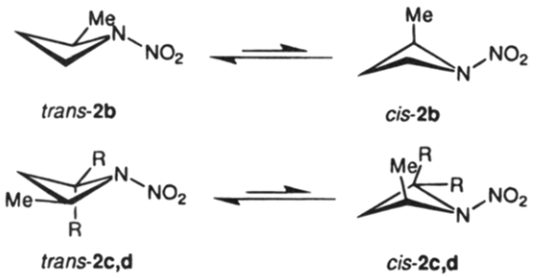
The nitrogen pyramid in nitroazetidines **2a-c** is more flattened than in nitroaziridines **3a–c** (*cf.* the out-of-plane angles α in Table 1). Correspondingly, an increase of the ring strain and of the contribution of the s function in the ring nitrogen n orbital leads to an increase of the nitrogen inversion barrier from 2.5 kcal/mol for *N*-nitroazetidine **2a** to 16.4 kcal/mol for *N*-nitroaziridine **3a**. At the same time, the opposite order is observed for the NN rotation barriers (12.7 kcal/mol for **2a** and 2.8 kcal/mol for **3a**[3]) because an increase of the s character of the n_N orbital (decrease of p character) decreases the capability of this orbital to participate in the n_N–π^*_{NO2} conjugation.

The greater values of the inversion barriers and the smaller ones of the rotation barriers for *N*-nitro-substituted azetidine **2a** and aziridine **3a** in comparison with the corresponding barriers for the *N*-nitroso derivatives[1c,e] testify to a higher σ acceptor ability and a poorer π acceptor ability of the nitro group in comparison with the nitroso group. In other words, oxidation of the nitroso group increases the effective electronegativity of the nitrogen atom and promotes depolarization of the NO bond compared to the nitroso group. As a consequence, in *N*-nitro-substituted heterocycles **2** and **3**, the ring nitrogen atom is more pyramidal and the NN bond is longer compared to the corresponding *N*-nitroso-substituted azetidines ($\Delta\alpha$ = *ca.* 12°, Δr(NN) = *ca.* 0.04 Å) and aziridines ($\Delta\alpha$ = *ca.* 3.5°, Δr(NN) = *ca.* 0.015 Å).

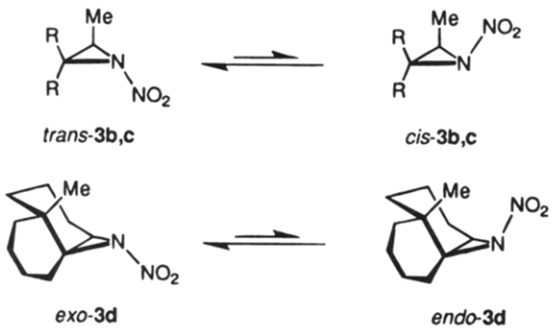
It was noted earlier[1e] that the azetidine ring puckering angle (β) is decreased when the double bonding between the ring nitrogen atom and a π-acceptor substituent is increased. The same dependence is also observed for *N*-nitroazetidine **2a**. The azetidine ring is completely planar in the inversion transition state TS_{inv}-**2a** (maximum NN double bonding), whereas in the rotation transition state TS_{rot}-**2a** with the orthogonal n_N and $\pi^*_{NO_2}$ orbitals, the ring has a considerable fold angle β. The ground state of **2a** with the pyramidal ring nitrogen, but with the coplanar n_N and $\pi^*_{NO_2}$ orbitals, occupies an intermediate position (Table 1). On the whole, in the ground states, *N*-nitroazetidines **2a-c** are characterized by the greater ring puckering angles (*ca.* 20°) than the analogous *N*-nitroso derivatives (*ca.* 11°) calculated at the same theoretical level.[1e] This effect on the ring folding is also a consequence of a comparatively poor π-acceptor ability of the nitro group.

The nitro group occupies the pseudoequatorial position in the nonplanar ring of all fully optimized structures of *N*-nitroazetidines **2a-c**. It has been established that the isomers with a pseudoaxial nitro group do not correspond to stationary points on the potential energy surface of the topomerization. Therefore, the methyl-substituted nitroazetidine **2b** can exist in the form of only two isomers—dipseudoequatorial *trans*-**2b** and pseudoequatorial—pseudoaxial *cis*-**2b** (Scheme 4). The latter is destabilized (Table 1) mainly by the steric interaction of the nitro and methyl groups. Assuming $\Delta S^\circ = 0$, the equilibrium ratio, *trans*-**2b**/*cis*-**2b**, is equal to 97.4:2.6 at 20 °C. In the case of 2,2,4-trisubstituted nitroazetidines **2c,d**, the isomer with the pseudoaxial 4-methyl group should be destabilized to a greater degree because of the additional steric repulsion of this group and the pseudo-

Scheme 4



Scheme 5



axial substituent R at C(2). Hence, the contribution of this isomer in an equilibrium mixture of the isomers of **2c,d** (Scheme 4) can be neglected.

The pseudoaxial position of the proton at C(2) in nitroazetidine **2b** and of the proton at C(4) in **2d** and, therefore, the pseudoequatorial position of the corresponding methyl groups are confirmed by the values of the vicinal spin coupling constants. These constants are equal to 7.7 ($^3J_{aa}$) and 8.5 Hz ($^3J_{ae}$) for **2b** and to 7.5 ($^3J_{aa}$) and 8.8 Hz ($^3J_{ae}$) for **2d**. It is known[1e,12] that for a pseudoequatorial proton of the azetidine ring, one coupling constant ($^3J_{ee}$) should be not more than 5 Hz. Indeed, in the case of nitroazetidine **2b**, the coupling constant $^3J_{ee}$ between the pseudoequatorial protons at C(3) and C(4) is equal to 4.7 Hz.

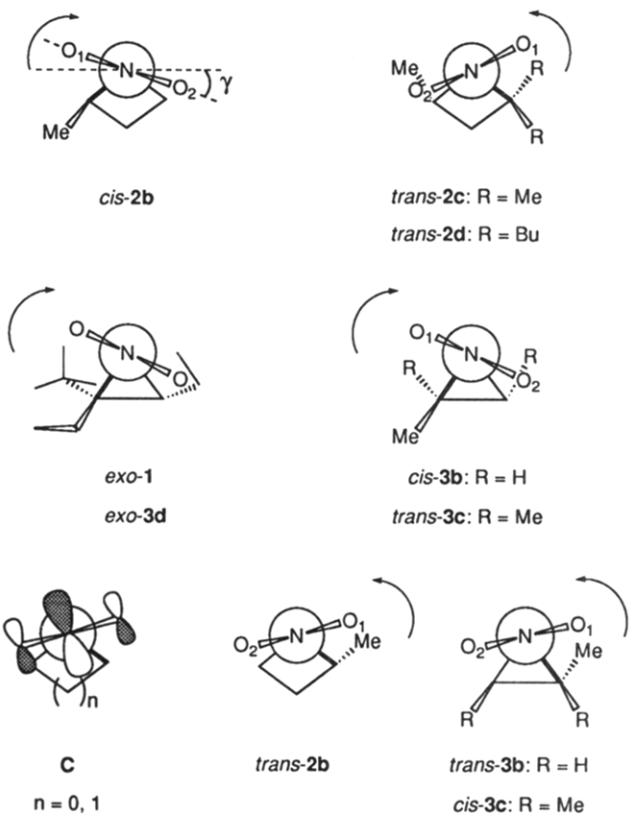
The calculated difference in energies of the *cis*- and *trans*-isomers of *N*-nitroaziridine **3b** is equal to 1.7 kcal/mol, which corresponds to the equilibrium ratio *trans*-**3b**/*cis*-**3b** = 95:5 (20 °C, assuming $\Delta S^\circ = 0$). For the trimethyl derivative **3c**, destabilization of the *cis*-isomer increases and the ratio *trans*-**3c**/*cis*-**3c** reaches 99.3:0.7. Hence, it can be supposed that the only invertomer of nitroaziridine **3d**, which is observed in the ^{1}H and ^{13}C NMR spectra, has the *exo*-orientation of the nitro group since, from the steric considerations, the *endo*-isomer of **3d** must be still less preferable than the *cis*-isomer in the pair of *cis,trans*-**3c**. It should be noted that according to the X-ray data,[2a] structurally similar nitroaziridine **1** exists also as the *exo*-invertomer (Scheme 5).

All stationary structures of the parent *N*-nitro-substituted azetidine **2a** and aziridine **3a** are achiral (Scheme 3). Unsymmetrical substitution in the ring forces twisting of the nitroamine chromophore and induces, thus, an intrinsic chirality of the latter.

According to the calculations, the greatest deviation from the symmetrical conformation about the NN bond (angle $\gamma = 4.8-12.0°$, Chart 1, Table 1) is observed for compounds *cis*-**2b** and **-3b** and *trans*-**2c** and **-3c**. The nitro group of these is subject to the steric influence of the *cis*-oriented 2-alkyl group. The experimental value[2a] of angle γ for nitroaziridine **1** is equal to 22.2°. Besides

(12) Fomichev, A. A.; Samitov, Yu. Yu.; Kostyanovsky, R. G. *Zh. Org. Khim.* **1981**, *17*, 1154−1162.

Chart 1



the steric factor, the interaction of the σ orbital of the CN bond (the heavy line in formula **C** and the others on Chart 1) with the antibonding $\pi^*_{NO_2}$ orbital can cause a torsional deformation of the pyramidal nitroamino group. The relative lengthening of the donor CN bond is a sign of this interaction. The influence of the similar $\sigma-\pi^*$ interaction on the twisting of the chromophore was noted earlier for *N*-acylaziridines,[1a] *N*-nitroso-substituted aziridines,[1c] and azetidines.[1e] The presence of alkyl substituents at the carbon atom enhances the donor ability of the CN bond,[1a,c,e] and therefore, the steric and electronic factors in *N*-nitroheterocycles *cis*-**2b** and **3b**, *trans*-**2c,d** and **3c**, and *exo*-**1** and **3d** work in the same direction.

Only the electronic factor causes the left-handed twisting of the nitroamine chromophore in compounds *trans*-**2b** and **3b** and *cis*-**3c** with the symmetrical closest spatial environment of the nitro group (Chart 1). In these cases, the deviation of the nitro group from the symmetrical conformation is substantially smaller (angle $\gamma = 0.15-1.85°$) than in corresponding isomers *cis*-**2b** and **-3b** and *trans*-**3c**. The greater value of twist angle γ in nitroaziridines **3b,c**, in comparison with nitroazetidines **2b,c** reflects, in addition, the greater donor ability of the CN bond of the three-membered ring. As we have noted above, the nitro group has a smaller π-acceptor ability than the nitroso group. This is a reason for the smaller NN twisting in *N*-nitroheterocycles **2** and **3** in comparison with the corresponding *N*-nitroso derivatives.[1c,e]

The above conformational analysis of *N*-nitroheterocycles **2,3** provides supporting evidence of the stereochemical lability of the pyramidal nitroamine chromophore and of the possibility of predictable induction of intrinsic chirality by carbon chiral centers. These data suggest that the shape of the CD spectra of nitroazetidine **2b** must be mainly determined by chiroptical properties of the dipseudoequatorial isomer *trans*-**2b** and the appearance of the CD spectra of **2d**—by properties of the

Table 2. Calculated Parameters[a] for the First Four Electronic Transitions of *N*-Nitroazetidines 2a–c and *N*-Nitroaziridines 3a–c

	GS-**2a** PCI	*cis*-**2b** PCI	*trans*-**2b** PCI	*trans*-**2c** PCI	GS-**3a** PCI	*cis*-**3b** PCI	*trans*-**3b** PCI	*cis*-**3c** PCI	*cis*-**3c** G92/CIS	*trans*-**3c** PCI	*trans*-**3c** G92/CIS
S_0-S_1											
descr	$n_O^- - \pi^*$	$n_O^- - \pi^*$	$n_O^- - \pi^*$	$n_O^- - \pi^*$	$n_O^- - \pi^*$	$n_O^- - \pi^*$	$n_O^- - \pi^*$	$n_O^- - \pi^*$		$n_O^- - \pi^*$	
E	6.46	6.49	6.42	6.49	5.89	5.93	5.93	6.11	5.79	6.06	5.76
[*R*]	0.00	−4.50	0.19	8.24	0.00	−5.89	0.18	0.1	0.2	−5.8	−5.8
f	0.0000	0.0002	0.0000	0.0009	0.0000	0.0002	0.0000	0.0000	0.0002	0.0002	0.0003
S_0-S_2											
descr	$n_O^+ - \pi^*$	$n_O^+ - \pi^*$	$n_O^+ - \pi^*$	$n_O^+ - \pi^*$	$n_O^+ - \pi^*$	$n_O^+ - \pi^*$	$n_O^+ - \pi^*$	$n_O^+ - \pi^*$		$n_O^+ - \pi^*$	
E	7.19	7.21	7.12	7.19	6.63	6.68	6.66	6.88	6.50	6.80	6.46
[*R*]	0.00	0.26	7.83	0.67	0.00	5.67	3.31	7.4	2.8	5.2	5.5
f	0.0049	0.0071	0.0049	0.0071	0.0038	0.0038	0.0040	0.0089	0.0076	0.0083	0.0061
S_0-S_3											
descr	$\pi_N - \pi^*$	$\pi_N - \pi^*$	$\pi_N - \pi^*$	$\pi_N - \pi^*$	$\pi_O - \pi^*$	$\pi_O - \pi^*$	$\pi_O - \pi^*$	$\pi_N - \pi^*$	$\pi_O - \pi^*$	$\pi_N - \pi^*$	$\pi_O - \pi^*$
E	8.45	8.33	8.37	8.31	8.72	8.71	8.80	8.32	7.98	8.45	7.99
[*R*]	0.00	8.72	−23.02	−8.94	0.00	15.20	8.15	−18.6	51.2	27.2	−32.5
f	0.1681	0.1948	0.1917	0.2007	0.0961	0.0758	0.1381	0.1676	0.2264	0.1909	0.2426
S_0-S_4											
descr	$\pi_O - \pi^*$	$\pi_O - \pi^*$	$\pi_O - \pi^*$	$\pi_O - \pi^*$	$\pi_N - \pi^*$	$\pi_N - \pi^*$	$\pi_N - \pi^*$	Rydberg	$\pi_N - \pi^*$	$\pi_O - \pi^*$	$\pi_N - \pi^*$
E	8.98	8.86	8.84	9.34	8.95	8.72	8.69	9.09	8.00	9.32	8.18
[*R*]	0.00	−6.09	−14.97	−2.61	0.00	2.52	−17.88	−7.7	−74.9	−47.8	39.0
f	0.0682	0.1321	0.1315	0.2284	0.1386	0.1194	0.0912	0.0621	0.2265	0.1308	0.2186

[a] The transition energies (*E*) are given in eV, the rotational strengths ([*R*]) in cgs × 10^{-40}, and the oscillator strengths (*f*) in cgs.

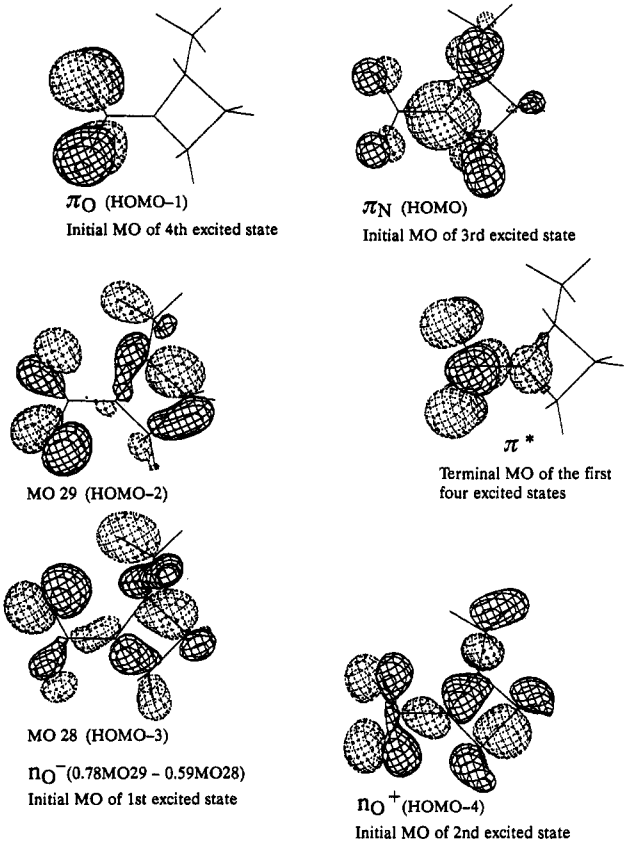


Figure 1. Five upper occupied molecular orbitals and the terminal orbital involved in the first four electronic transitions of (2*R*)-2-methyl-1-nitroazetidine **2b**; contour 0.05.

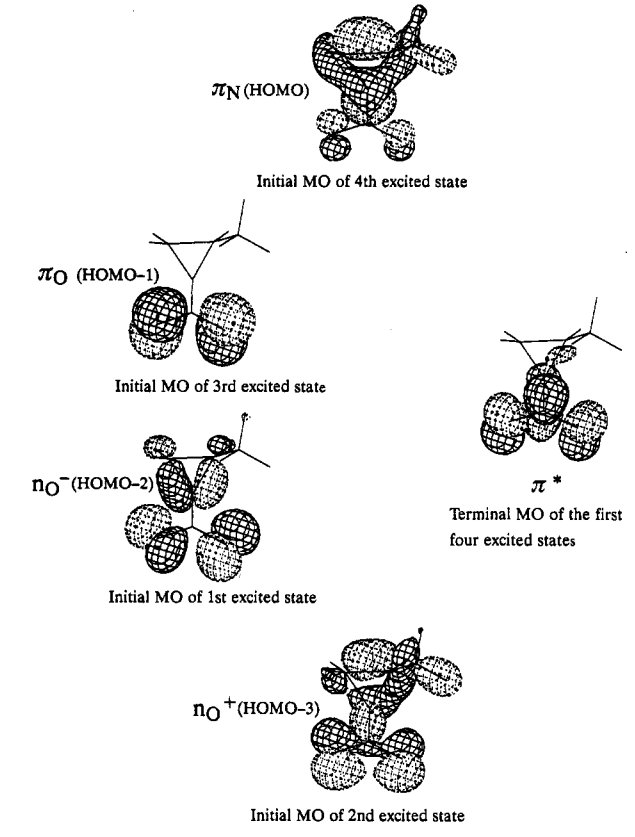


Figure 2. Four upper occupied molecular orbitals and the terminal orbital involved in the first four electronic transitions of *cis*-(2*R*)-2-methyl-1-nitroaziridine **3b**; contour 0.05.

isomer *trans*-**2d**. The latter is modeled by compound *trans*-**2c**. Similarly, nitroaziridine *trans*-**3c** and, to some extent, *cis*-**3b** are adequate computational models for interpretation of the CD spectra of nitroaziridine **3d**.

Chiroptics. According to the calculations (Table 2), the nitroazetidine and nitroaziridine chromophores have the similar orbital origin of the first four electronic transitions. All the transitions are to the antibonding π^* orbital of the nitroamino groups (Figures 1 and 2). An antisymmetrical combination of the n orbitals of the oxygen atoms (n_O^-) with an out-of-phase admixing of the orbitals of the CN bonds is the initial orbital of the first transition. The initial orbital of the second transition is considerably delocalized over the framework of the *N*-nitroheterocycle, but a symmetrical combination of the n orbitals of the oxygen atoms (n_O^+) is the principal component of this MO. Both combinations, i.e., n_O^- and n_O^+, lie close to the plane of the nitro group (Figures 1 and 2), and the electronic transitions in which they participate are electric dipole forbidden and are characterized by very small oscillator strengths (Table 2). This is especially true for the first transition for the

Table 3. CD and UV Spectra of *N*-Nitroazetidines 2b,d and *N*-Nitroaziridine 3d

			λ_{max}, nm ($\Delta\epsilon$ or ϵ)	
cmpd	method	solvent	band I	band II
2b	CD	heptane	250 (0.703)	218 (−3.32)
		MeCN	255 (0.496)	223sh (−2.4)
		MeOH	257 (0.404)	220sh (−2.5)
	UV	heptane		229 (6530)
		MeOH		241 (6750)
2d	CD	heptane	274 (2.803)	232 (−7.43)
		MeCN	276 (3.038)	232 (−6.37)
		MeOH	275 (2.803)	230 (−6.12)
	UV	heptane		239 (5060)
		MeOH		246 (6631)
3d	CD	heptane	298 (−2.000)	232 (5.70)
		MeCN	300 (−2.052)	242 (5.01)
		MeOH	299 (−2.349)	239 (4.88)
	UV	heptane		232 (4080)
		MeOH		238 (3760)

symmetrical molecules of **2a** and **3a** and for the weakly NN-twisted structures, *trans*-**2b** and -**3b**. Thus, the first two electronic transitions cannot practically be observed in the experimental UV spectra of *N*-substituted azetidines and aziridines.

The next two transitions are electric dipole allowed according to the calculated oscillator strengths (Table 2) and can be described as the $\pi_N-\pi^*$ and $\pi_O-\pi^*$ transitions because both initial orbitals have π symmetry. One of them is mainly localized on the ring nitrogen atom and the other only on the oxygen atoms (Figures 1 and 2). For nitroazetidines **2a-c**, the $\pi_N-\pi^*$ transition has a lower energy than the $\pi_O-\pi^*$ transition, whereas in the case of simple nitroaziridines **3a,b**, the order is opposite owing mainly to the increase of the $\pi_N-\pi^*$ transition energy. The latter is apparently caused by the greater s-character of the principal n_N component of the π_N orbital of the nitroaziridine chromophore and by mixing the component with orbitals of the three-membered ring (Figure 2). Indeed, the HOMO (π_N) energy of nitroaziridine **3a** is lower by 0.49 eV than the energy of the corresponding orbital of nitroazetidine **2a**. The sequence of the $\pi_N-\pi^*$ transition energies of trimethyl aziridines *cis,trans*-**3c** depends on the calculation method. The method (G92/CIS) using a more expanded basis set predicts the lower energy for the $\pi_O-\pi^*$ transition rather than the $\pi_N-\pi^*$ transition. Thus, it seems reasonable to assume that the main band, observed in the UV spectra of nitroazetidines **2b,d**, is mainly caused by the $\pi_N-\pi^*$ transition and in the UV spectra of nitroaziridine **3d** by the $\pi_O-\pi^*$ transition. The $\pi-\pi^*$ origin of this band is supported by the values of extinction coefficients (ϵ) and by the bathochromic shift in a polar solvent (MeOH) (Table 3).

Unlike the UV spectra, the CD spectra of *N*-nitroheterocycles **2b,d** and **3d** contain two absorption bands (Figure 3, Table 3). Evidently, the additional long-wavelength band (band I) is caused by one or both magnetic dipole allowed transitions $n_O^- - \pi^*$ and $n_O^+ - \pi^*$. The short-wavelength dichroic band (band II) is observed in the same region, i.e., 230−240 nm, as the band of isotropic absorption and, consequently, has the same $\pi-\pi^*$ origin.

According to the calculations (Table 2), the ratio of the values of the rotational strengths of the $n_O-\pi^*$ transitions of nitroazetidines **2b,c** depends, substantially, on the degree of the torsional deformation of the chromophore. For weakly twisted *trans*-**2b**, the rotational strength of the $n_O^- - \pi^*$ transition is smaller than one of

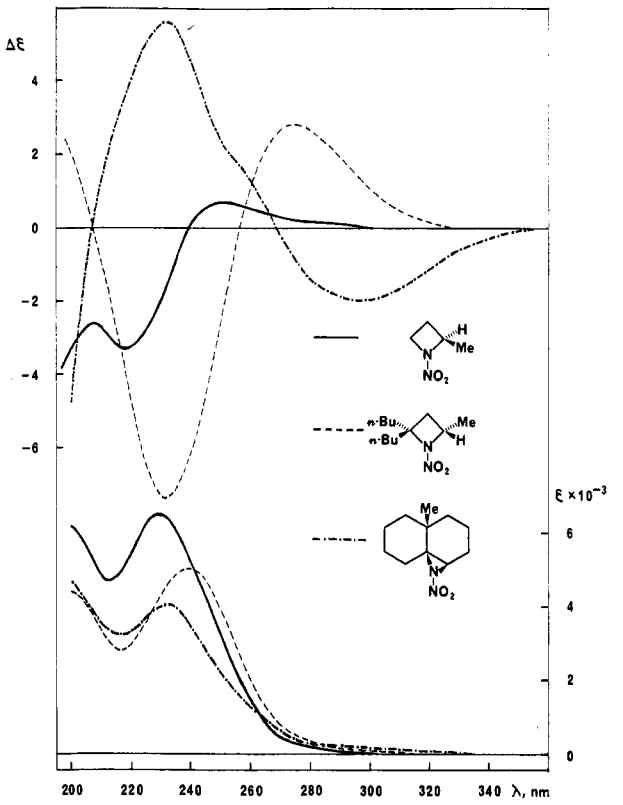


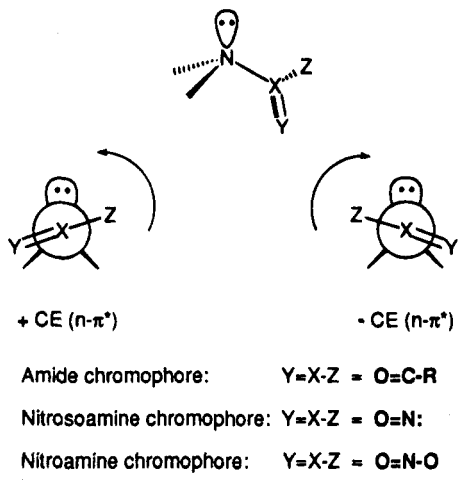
Figure 3. CD and UV spectra of *N*-nitroazetidines **2b,d** and *N*-nitroaziridine **3d** in heptane.

the $n_O^+ - \pi^*$ transition, whereas the more twisted compounds *cis*-**2b** and *trans*-**2c** are characterized by the reverse ratio of the values of the rotational strengths of these transitions. Therefore, it can be concluded that the main contribution in band I of nitroazetidine **2b** is made by the higher energy $n_O^+ - \pi^*$ transition and in band I of **2d** by the $n_O^- - \pi^*$ transition. Hence, the considerable short-wavelength shift of band I in the CD spectra of **2b** in comparison with band I of **2d** (Table 3, Figure 3) becomes clear. Bands I have the positive signs as the calculated rotational strengths of the corresponding electronic transitions of nitroazetidines *trans*-**2b,c**.

It follows from comparison of the calculated parameters of both $n_O-\pi^*$ transitions of the model *N*-nitroaziridines *cis*-**3b** and *trans*-**3c** with the experimental CD spectra of **3d** that the observed negative band I is caused by the $n_O^- - \pi^*$ transition; the higher energy $n_O^+ - \pi^*$ transition with the positive rotational strength is revealed as the long-wavelength shoulder of positive band II in heptane (Figure 3) or is absorbed by the latter in methanol and acetonitrile owing to increasing of the $\pi_O-\pi^*$ transition wavelength. The bathochromic shift of band I in the CD spectra of nitroaziridine **3d** relative to band I of nitroazetidine **2d** is a consequence of lowering of the terminal π^* orbital energy owing to weakening of the amide type conjugation[1] in the nitroaziridine chromophore. The calculated energies of the $n_O^- - \pi^*$ transition in *N*-nitroaziridines **3** are also lower than ones in *N*-nitroazetidines **2** (Table 2).

The signs of dichroic band II in the CD spectra of *N*-nitroheterocycles **2b,d** and **3d** are in agreement with the calculated rotational strength signs of the lower energy $\pi-\pi^*$ transition (S_0-S_3) of the model compounds *trans*-**2b,c** and -**3c** and *cis*-**3b**. At first glance, the calculated result for *trans*-**3c** by the G92/CIS method is an exception. This method gives a negative sign of the third transition rotational strength versus the positive

Chart 2



sign of band II in the CD spectra of **3d**. However, the calculation predicts also that the fourth excited state ($\pi_N-\pi^*$ transition) is nearly degenerate and has a greater positive rotational strength. Superposition of the bands of the $\pi_O-\pi^*$ and $\pi_N-\pi^*$ transitions must afford positive dichroic band II.

It is apparent from the calculated and experimental data that only the rotational strength signs of the $n_O^- - \pi^*$ and $\pi_N-\pi^*$ transitions correlate with the intrinsic chirality of the nonplanar nitroamine chromophore. *N*-Nitroheterocycles *trans*-**2b,c,d** and **-3b** and *cis*-**3c** with the left-handed chromophore chirality are characterized by the positive rotational strength of the $n_O^- - \pi^*$ transition and by the negative one of the $\pi_N-\pi^*$ transition. The opposite is true for right-handed *cis*-**2b** and **-3b**, *trans*-**3c**, and *exo*-**3d**. However, the correlation for the $\pi_N-\pi^*$ transition is apparently fortuitous because the rotational strength of this transition is actually decreased from weakly NN twisted *trans*-**2b** and **-3b** and *cis*-**3c** to strongly twisted *cis*-**2b** and **-3b** and *trans*-**2c** and **3c** (Table 2). It is more likely that the sign of the rotational strength of the $\pi_N-\pi^*$ transition is determined by the absolute configuration of the ring nitrogen atom, the n orbital of which is the principal component of the initial MO of this transition. Indeed, all compounds (*cis*-**2b** and **-3b**, *trans*-**3c**) with (*S*)-configuration of the nitrogen have the positive sign and (1*R*)-*trans*-**2b,c** and **-3b,c** the negative one. In practice, it should be difficult to use the CE sign of the $\pi_N-\pi^*$ transition for stereochemical considerations of strongly nonplanar nitroamines such as *N*-nitroaziridines because this CE cannot be observed in the CD spectra or is overlapped by the CE of the $\pi_O-\pi^*$ transition. In this respect, the longer wavelength CE of the $n_O^- - \pi^*$ transition has the advantage, though for weak-twisted *N*-nitroazetidines this CE can be masked by the more intensive CE of the $n_O^+ - \pi^*$ transition. Nevertheless, the sign of the rotational strength of the $n_O^- - \pi^*$ transition has the direct correlation with the chromophore intrinsic chirality because the rotational strength is increased (Table 2) with the increase of the chromophore NN-torsional deformation (angle γ, Table 1). In principal, according to the orbital origin, this transition is similar to the $n-\pi^*$ transitions of other nonplanar nitrogen-containing chromophores, i.e., amide[1a,d] and nitrosoamine[1b,c,e] ones, and the above-mentioned connection of the CE sign of the $\pi_O-\pi^*$ transition with the intrinsic chirality of the nonplanar nitroamine chromophore is the same as in the cases of these chromophores (Chart 2).

It should be noted that sector rules which were offered for *N*-nitropyrrolidines[13a] and piperidines[13a,b] cannot be used for the intrinsically chiral nitroamine chromophore because these rules are based on the existence of the local planes of symmetry of the nitroamino group.

Conclusions

The nitro group is a better internal electronic σ-acceptor but a poorer π-acceptor than the acyl and nitroso groups. Therefore, *N*-nitro-substituted azetidines and aziridines are characterized by higher pyramidality of the ring nitrogen atom and have higher nitrogen inversion barriers and lower rotation barriers in comparison with *N*-acyl[1a] and *N*-nitroso derivatives.[1c,e] The calculated topomerization barriers of the parent compounds indicate stereochemical lability of the pyramidal nitroamino group and, correspondingly, possibility of thermodynamic control of population of stereoisomers of *N*-nitroazetidines and aziridines, containing alkyl substituents. The conformational equilibrium of the α-monoalkyl-substituted compounds is strongly shifted toward the isomers with *trans*-orientation of the nitro and α-monoalkyl group; *N*-nitroazetidines are characterized by the puckered ring, and the groups are in the pseudoequatorial positions. The calculated equilibrium ratios and values of the optical rotational strengths permit us to assume that the shapes of the CD curves of *N*-nitroazetidines and aziridines are determined by chiroptical properties of the major isomers.

The closest asymmetrical environment causes the torsional deformation of the pyramidal nitroamine chromophore and thus induces the intrinsic chirality of the latter. It has been established that from a set of the electronic transitions ($n_O^- - \pi^*$, $n_O^+ - \pi^*$, $\pi_N-\pi^*$, and $\pi_O-\pi^*$) which can be observed in CD spectra of *N*-nitroazetidines and aziridines in solutions, only the parameters of the $n_O^- - \pi^*$ transition are sensitive to the intrinsic chirality of the chromophore. The CE of this transition is revealed in the region 270–300 nm at a sufficiently high NN-twisting of the chromophore. Weakening of the amide-like conjugation at increasing of the ring nitrogen pyramidality from the nitroazetidine chromophore to the nitroaziridine one causes a noticeable bathochromic shift (*ca.* 20 nm) of the CE. The CE sign obeys a spiral rule which was established for the nonplanar intrinsically chiral amide[1a,d] and nitrosoamine[1b,c,e] chromophores.

Experimental Section

(2*R*)-1-Nitro-2-methylazetidine (2b). A solution of *N*-nitrosoazetidine (+)-**4**[1e] (0.501 g, 5 mmol) in CH_2Cl_2 (5 mL) was added dropwise to a solution of trifluoroperacetic acid[7a] (10 mmol) in CH_2Cl_2 (3 mL) with stirring. The reaction mixture was stirred at rt for 1 h, refluxed for 1 h, cooled, washed with cold water and 10% aqueous $NaHCO_3$ (2 × 10 mL), and dried over $CaCl_2$. The solvent was evaporated in vacuo, and the residue was distilled, providing *N*-nitroazetidine **2b** (0.45 g, 77%): bp 46–47 °C (0.25 mm), $[\alpha]^{20}_D$ −85.7° (*c* 1.9, $CHCl_3$); ^1H NMR (400 MHz) in $CDCl_3$ (*J*, Hz): δ 1.55 (3H, d, ^3J = 6.3), 1.89 (1H, m, ^2J = −11.0, ^3J = 7.7, 8.6), 2.27 (1H, m, ^2J = −11.0, ^3J = 4.7, 8.5), 4.20 (1H, m, ^2J = −8.5, ^3J = 4.7, 8.6), 4.24 (1H, m, ^2J = −8.5, ^3J = 8.5, 8.6), 4.69 (1H, m, ^3J = 6.3, 7.7, 8.5). Anal. Calcd for $C_4H_8N_2O_2$: C, 41.35; H, 6.9; N, 24.1. Found: C, 41.5; H, 6.6; N, 24.2.

(4S)-1-Nitro-2,2-dibutyl-4-methylazetidine (2d). A solution of trifluoroperacetic acid[7a] (2 mmol) in CH_2Cl_2 (3 mL) was added dropwise to a rapidly stirred solution of *N*-nitrosoazetidine (+)-**5**[1e] (85 mg, 0.4 mmol) in CH_2Cl_2 (10 mL) containing

(13) (a) Polonski, T.; Prajer, K. *Tetrahedron Lett.* **1975**, 3539–3542. (b) Ripperger, H. *Z. Chem.* **1977**, *17*, 177–178.

suspended Na_2CO_3 (636 mg, 6 mmol), and the reaction mixture was refluxed for 1 h and cooled. The precipitate was filtered off and washed with CH_2Cl_2. The filtrate was concentrated in vacuo, and the residue was purified by flash chromatography (silica gel 60, 230–400 mesh, 8% EtOAc in light petroleum ether) to give 84 mg (92%) of *N*-nitroazetidine **2d**: $[\alpha]^{20}_D$ +47.6° (*c* 2.6, heptane); ^{1}H NMR (200 MHz) in CDCl3 (*J*, Hz) δ 0.92 and 0.94 (6H, dt, ^3J = 6.8), 1.26–1.45 (8H, m), 1.49 (3H, d, ^3J = 6.2), 1.68 (1H, dd, ^2J = −10.9, ^3J = 7.5), 1.77–1.97 (4H, m), 2.14 (1H, dd, ^2J = −10.9, ^3J = 8.8), 4.51 (1H, m). Anal. Calcd for $C_{12}H_{24}N_2O_2$: C, 63.1; H, 10.6; N, 12.3. Found: C, 63.0; H, 10.7; N, 12.1.

(*R*)-10-Methyl-Δ^{1,9}-octalin (7), bp 84–86 °C (25 mm) [lit.[8b] bp 86–88 °C (26 mm)], $[\alpha]^{20}_D$ −100.6° (*c* 2.4, $CHCl_3$), was prepared from (*R*)-10-methyl-1(9)-octal-2-one (**6**)[8a] (ee *ca.* 76%) with total yield 45% according to the procedures of Marshall and Hochstetler.[8b]

(9*R*,10*R*)-1-Oximino-9-chloro-10-methyldecalin ((*E*)-8). The procedure developed by Haire and Boswell[5] was used to prepare (*E*)-**8**. The crude material was purified by crystallization with hexane to afford oxime (*E*)-**8** as white crystals: yield 35%; mp 121–122 °C (lit.[5] mp 128–132 °C for racemic (*E*)-**8**); $[\alpha]^{20}_D$ −105.4° (*c* 1.6, $CHCl_3$); ^{1}H NMR (200 MHz) in $CDCl_3$ (*J*, Hz) δ 1.02 (3H), 1.08–1.25 (2H, m), 1.49–2.15 (10H, m), 2.44 (1H, m, ^2J = −15.1, ^3J = 8.9, 10.4), 3.27 (1H, m, ^2J = −15.1, ^3J = 1.2, 4.5), 8.68 (1H, br s). Anal. Calcd for $C_{11}H_{18}ClNO$: C, 61.2; H, 8.4; N, 6.5. Found: C, 61.0; H, 8.2; N, 6.6.

(α*R*,9*R*,10*R*)-*O*-(*N*-(α-Methylbenzyl)carbamoyl)-1-oximino-9-chloro-10-methyldecalin (9). A solution of oxime (*E*)-**8** (32 mg, 0.149 mmol) and (*R*)-(+)-α-methylbenzyl isocyanate (22 mg, 0.15 mmol) in dry CH_2Cl_2 (1 mL) was kept at rt for 5 days, washed with 5% aqueous HCl and saturated aqueous $NaHCO_3$ solutions, dried over $MgSO_4$, and concentrated in vacuo. There was obtained 51 mg (94%) of **9** as a slightly yellowish oil which was identified on the ^{1}H NMR spectrum: ^{1}H NMR (400 MHz) in $CDCl_3$ (*J*, Hz) δ 1.00 and 1.04 (3H, ds), 1.21 (2H, m), 1.56 and 1.57 (3H, dd, ^3J = 6.9), 1.59–2.10 (10H, m), 2.61 (1H, m, ^2J = −15.3, ^3J = 8.3, 12.6), 3.35 (1H, br dd, ^2J = −15.3, ^3J = 5.1, < 1.0), 5.01 (1H, m, ^3J = 6.9), 6.45 (1H, br d, ^3J = 6.9), 7.26–7.44 (5H, m). The diastereomer ratio was found to be ca. 88:12 by integration of the singlets at 1.00 (major diastereomer) and 1.04 ppm (minor diastereomer).

(9*R*,10*R*)-1-Nitrimino-9-chloro-10-methyldecalin (10). Nitrosyl chloride (3.9 g, 60 mmol) was slowly bubbled in a solution of oxime (*E*)-**8** (3.93 g, 20 mmol) and pyridine (4.75 g, 60 mmol) in dry CH_2Cl_2 (300 mL) with stirring and cooling (−20 °C). The reaction mixture was stirred at 0 °C for 3 h and washed with ice-cold water, 5% aqueous HCl, and brine. After being dried over $MgSO_4$, the solution was concentrated in vacuo and the residue was purified by column chromatography (silica gel 60, 230–400 mesh, 10% $CHCl_3$ in hexane) and further crystallization with pentane at −8 °C to afford 2.25 g (46%) of nitrimine **10** as white plates: mp 92–93 °C (lit.[5] mp 61–62 °C for racemic **10**); $[\alpha]^{20}_D$ −128.5° (*c* 1.2, heptane); ^{1}H NMR (200 MHz) in $CDCl_3$ (*J*, Hz) δ 1.10 (3H), 1.16–1.36 (2H, m), 1.51–2.20 (10H, m), 2.41 (1H, m, ^2J = −15.0, ^3J = 1.3, 4.1), 3.06 (1H, m, ^2J = −15.0, ^3J = 8.8, 10.8). Anal. Calcd for $C_{11}H_{17}ClN_2O_2$: C, 54.0; H, 7.0; N, 11.45. Found: C, 54.1; H, 7.1; N, 11.4.

(1*R*,9*R*,10*R*)-1-Nitramino-9-chloro-10-methyldecalin (11). The procedure developed by Haire and Boswell[5] was used to prepare **11**. The crude material was purified by crystallization with hexane at −10 °C to afford nitramine **11** (77%) as a white crystallosolvate with dioxane (1:0.5 mol/mol): mp 79–83 °C (lit.[5] mp 136 °C for pure racemic **11**); $[\alpha]^{20}_D$ −107.5° (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz) in 5% CD_3OD in $CDCl_3$ (*J*, Hz) δ 1.06–1.14 (2H, m), 1.21 (3H), 1.53–2.12 (11H, m), 2.64 (1H, m, ^2J = −13.0, ^3J = 5.3, 8.1, 10.6), 3.72 (4H), 4.65 (1H, br d, ^3J = 5.3, < 1.0).

(1*R*,9*R*,10*R*)-10-Methyl-1.9-(*N*-nitroaziridino)decalin (3d). The procedure of Haire and Boswell[5] was followed. To a stirred solution of the complex of nitramine **11** with dioxane (1:0.5 mol/mol, 582 mg, 2 mmol) in dry THF (30 mL) under argon was added BuLi (2.5 M in hexane, 0.8 mL, 2 mmol). The reaction mixture was refluxed for 1 h, kept at rt for 24 h, and diluted with CH_2Cl_2 (120 mL). The mixture was washed with water, dried over $MgSO_4$, and concentrated in vacuo. The product was extracted from the residue with pentane, and the extract was filtered through a $MgSO_4$ plug and concentrated in vacuo. The crude material was purified by slow sublimation at 25 °C (0.1 mm) to afford 177 mg (42%) of *N*-nitroaziridine **3d** as soft slightly yellowish crystals: mp 38–42 °C (racemic **3d** was described[5] as an oil); $[\alpha]^{20}_D$ −30.7° (*c* 0.9, heptane); ^{1}H NMR (200 MHz) in $CDCl_3$ (*J*, Hz) δ 0.73–1.93 (12H, m), 1.22 (3H), 2.16 (2H, m), 3.12 (1H, br d, ^3J = 5.6); ^{13}C NMR (100 MHz) in $CDCl_3$ (^1J, Hz) δ 15.54 (t, 130.8), 21.12 (t, 126.4), 21.96 (t, 129.3), 23.81 (q, 125.0), 25.08 (t, 125.7), 28.77 (t, 127.9), 32.37 (s), 33.99 (t, 127.9), 50.93 (d, 167.1), 59.31 (s). Anal. Calcd for $C_{11}H_{18}N_2O_2$: C, 62.8; H, 8.6; N, 13.3. Found: C, 63.1; H, 8.7; N, 13.2.

Computational Methods. The structures of the nitro compounds **2a–c** and **3a–c** were fully optimized at the Hartree–Fock level using procedures implemented in the Gaussian 92 system of programs[14] and the internal 6-31G* basis set. In the case of **2a** and **3a**, transition structures for rotation and inversion were also located. Harmonic frequency analysis verified the nature of the stationary points as minima (all real frequencies) or as transition structures (one imaginary frequency). Relative energies were estimated at the HF/6-31G* level. For the purpose of Boltzmann population analysis, entropy differences between conformations were assumed to be zero.

For all species, chiroptical properties were calculated using the 6-31+G* basis set at the 6-31G* geometries. The use of the diffuse s and p functions designated by the "+" is desirable for a more accurate description of the excited singlet states. For chiroptical properties, the PCI or Gaussian 92 (G92/CIS) programs were used. The PCI program determines optical rotatory strengths and dipole oscillator strengths from dipole transition moments which are correct to first order in Rayleigh–Schrödinger perturbation theory. Both the ground and excited states are partitioned into zero- (strongly interacting) and first-order (weakly interacting) contributions. Only single excitation CI is carried out for the excited states, while electron correlation of the ground state wave function is taken into account in the form of doubly excited configurations as first order corrections to the zero-order Hartree Fock single determinantal wavefunction. For technical reasons, PCI is limited to a window of 15 occupied and 50 unoccupied orbitals. This is not a serious limitation for smaller molecules such as **2a** and **3a**, but may be so for larger molecules like **2c** and **3c**. PCI has been extensively used,[1,15] and the theory is described in detail elsewhere.[16] On the other hand, a CIS calculation uses a window of all valence occupied and unoccupied orbitals but does not include the ground state correlation contribution. Molecular orbitals of the ground and excited states are displayed as modified Jorgensen–Salem plots.[17]

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