Conformational and Chiroptical Properties of *N*-Nitrosoazetidines

G. V. Shustov[†] and A. Rauk*[,‡]

Contribution from the Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russia, and Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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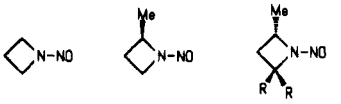
Abstract: Optically active *N*-nitrosoazetidines, containing the isolated nitrosoazetidine chromophore, i.e. (2*R*)-1-nitroso-2-methylazetidine (**2**) and (4*S*)-1-nitroso-2,2-dibutyl-4-methylazetidine (**5**), are synthesized, and their ^{1}H NMR, CD, and UV spectra are studied. A topomerization mechanism, structural features, and chiroptical properties of the individual isomers of the parent 1-nitrosoazetidine (**1**) and its (2*R*)-2-methyl, (4*R*)-2,2,4-trimethyl, and (4*S*)-2,2-diethyl-4-methyl derivatives **2**−**4** are studied theoretically by means of non-empirical quantum chemical calculations. It is shown that the CD spectra of *N*-nitrosoazetidines can be interpreted on the basis of the two-position *Z*,*E*-equilibrium, taking into account the nonplanarity of the nitrosoazetidine chromophore. The Cotton effect sign of the n−π* transition at 380 nm is determined by the intrinsic chirality of the chromophore and obeys a spiral rule.

Introduction

Secondary *N*-nitrosoamines are of widespread interest because of their high biological activity.[1] Circular dichroism (CD) spectroscopy in combination with NMR spectroscopy is a principal method for the study of the stereochemistry of these compounds.[2] Chiral rules connecting the Cotton effect (CE) sign of the n−π* transition of the nitrosoamine chromophore with the absolute stereochemistry of the molecule have been offered. These are Snatzke−Gaffield[2a−c] and Polonski[2a,e] sector rules for virtually planar *N*-nitrosoamines and a spiral rule[2f,g] for nonplanar ones.

In the series of studied heterocyclic *N*-nitrosoamines, i.e. *N*-nitroso-substituted piperidines,[2a−c] pyrrolidines,[2a,c−e] and aziridines,[2f,g] *N*-nitrosoazetidines are practically absent, except (2*S*)-1-nitrosoazetidine-2-carboxylic acid.[2c] Nevertheless, *N*-nitrosoazetidines are worthy of more detailed study of their conformational and chiroptical properties because they are evidently an intermediate case between virtually planar *N*-nitrosopyrrolidines and highly pyramidal *N*-nitrosoaziridines. Indeed, the barrier of rotation about the NN bond in the parent *N*-nitrosoazetidine (**1**) (19.6 kcal mol^{-1})[3a] is lower than the barriers of rotation for the majority of planar nitrosoamines (23−25 kcal mol^{-1}).[3b] Besides, data[4] of semiempirical quantum chemical calculations of compound **1** reveal little deviation from the planar configuration for the azetidine nitrogen atom.

We have studied *N*-nitrosoazetidines **1**−**5** that possess the isolated nitrosoazetidine chromophore, unlike the 1-nitrosoazetidine-2-carboxylic acid. (2*R*)-1-Nitroso-2-methylazetidine (**2**)



1 **2** **3** (R = Me) **4** (R = Et) **5** (R = Bu)

and (4*S*)-1-nitroso-2,2-dibutyl-4-methylazetidine (**5**) have been studied experimentally. For compounds **1**−**4**, non-empirical quantum chemical calculations have been carried out.

Results and Discussion

Synthesis. N-Unsubstituted azetidines **9** and **10**, precursors of *N*-nitrosoazetidines **2** and **5**, were synthesized on the basis of diastereomers of *N*-(1′-phenylethyl)-3-aminobutyric acid **6** (Scheme 1). Separation of these diastereomers and assignment of their absolute configurations were described earlier.[5] The absolute configurations of azetidinones **7** and **8** were also established independently.[6]

We have modified a procedure[7] of cyclization of amino acids **6** to azetidinones **7**. With the use of a lower boiling solvent, CH_2Cl_2 instead of benzene, and a stronger base, Et_3N rather than *N*,*N*-dimethylaniline,[7] one can carry out the reaction at lower temperature. Diastereomerically pure azetidinones **7** are obtained in high yield. All further reactions are also carried out in sufficiently mild conditions and without affecting the chiral center. For the introduction of the butyl groups in the α-position of the azetidinone ring, the amide group of azetidi-

[†] Russian Academy of Sciences.

[‡] University of Calgary.

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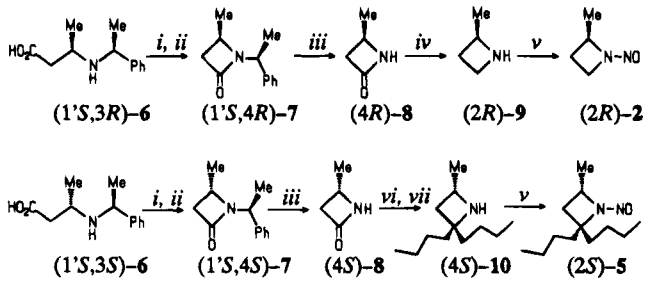
Scheme 1[a]



[a] Reagents: (*i*) $SOCl_2$; (*ii*) Et_3N; (*iii*) Na, NH_3; (*iv*) $LiAlH_4$; (*v*) $NaNO_2$, HCl; (*vi*) $Et_3O^+BF_4^-$; (*vii*) BuLi.

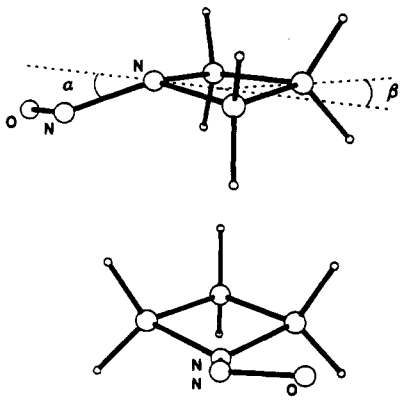


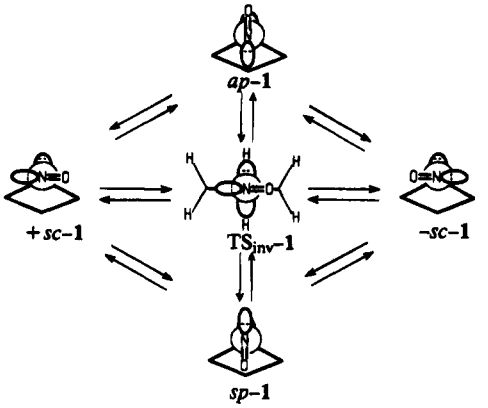
Figure 1. 6-31G* structure of the −*sc* rotamer of 1-nitrosoazetidine (**1**) (see Table 1).

none **8** was activated by O-ethylation with triethyloxonium tetrafluoroborate.[8] It should be noted that *N*-nitrosoazetidines **5** is obtained in high yield after treatment of N-unsubstituted azetidine **10** with an excess of $NaNO_2$ in dilute hydrochloric acid at 20 °C, whereas considerable product decomposition was observed when we used a typical nitrosation procedure[9] of azetidines, i.e. by heating at 80 °C with $NaNO_2$ in 50% aqueous acetic acid.

Conformation. The fully optimized structures of *N*-nitrosoazetidines **1**−**4** are characterized by the pyramidal azetidine nitrogen, the nonplanar ring, and the pseudoequatorial orienation of the nitroso (Figure 1) and monomethyl groups (Table 1). The isomers with a pseudoaxial orientation of one or both groups are not minima of the potential energy surface of the topomerization of *N*-nitrosoazetidines **1**−**4**.

The chiral synclinal (±*sc*) conformation of the nitroso group, which permits maximum possible overlap of the n_N and π^*_{NO} orbitals is realized in all cases. For the parent *N*-nitrosoazetidine

Scheme 2



(**1**), it has been shown that the antiperiplanar and synperiplanar conformations, *ap*- and *sp*-**1**, are the transition states for the rotation about the NN bond (Scheme 2, Table 1). The lowest barrier of rotation through *ap*-**1** (17.4 kcal mol^{-1}, Table 1) is close to the experimental value,[3a] 19.6 kcal mol^{-1}. Destabilization of *sp*-**1** relative to *ap*-**1**, as in the case of *N*-nitrosoaziridine,[2g] is caused mainly by the interaction of the eclipsed nitrogen lone pair. The calculated values of the rotational barriers for *N*-nitrosoazetidine (**1**) (Table 1) are substantially greater than the corresponding values calculated for the parent *N*-nitrosoaziridine (4.0 and 7.1 kcal mol^{-1}, respectively)[2g] at the same level. This is because incorporation of the tricoordinated nitrogen of the nitrosoamino group into the four-membered ring weakens the $n_N-\pi^*_{NO}$ conjugation in a smaller degree than does its introduction into a three-membered ring. The azetidine nitrogen pyramidality for *sc*-rotamers **1**−**4** is also relatively low; the out-of-plane angles (α, Figure 1) are 10.0−28.9° vs 51.4−54.5° for the same rotamers of *N*−nitrosoaziridines.[2g] Correspondingly, *N*-nitrosoazetidine (**1**) has a very low nitrogen inversion barrier (Table 1).

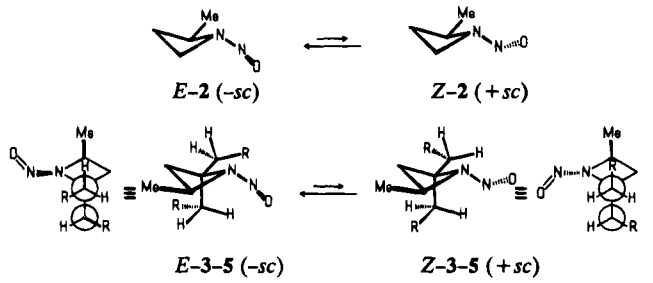
The ring puckering angles (β), calculated for the ground states of *N*-nitrosoazetidines **1**−**4** (Table 1), are close to the experimental angle for 1-cyano-2-methylazetidine (14°)[10a] and are noticeably different from the angles (30−34°) that are typical for N-unsubstituted and *N*-alkylazetidines.[10] Evidently, an increase of the double bonding between the ring nitrogen atom and a π−acceptor substituent, i.e. the amide−type conjugation, promotes ring flattening. This effect is observed especially well for such extreme structures of *N*-nitrosoazetidine (**1**) as the rotation transition states, *ap*- and *sp*-**1**, and the inversion transition state, **TS**$_{inv}$−**1**. In the first two cases, the n_N and π^*_{NO} orbitals are orthogonal and the angle β approaches 30°, whereas

Table 1. Selected Geometrical Parameters,[a] Dipole Moments,[b] and Relative Energies[c] of the Stationary Structures of *N*−Nitrosoazetidines **1**−**4** at the RHF 6-31G* Level

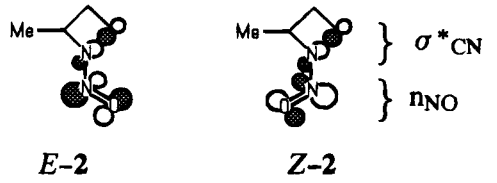
	sc-**1**	*ap*-**1**	*sp*-**1**	**TS**$_{inv}$-**1**	*E*-**2**	*Z*-**2**	*E*-**3**	*Z*-**3**	*E*-**4**[d]	*Z*-**4**[d]
NO	1.191	1.163	1.166	1.197	1.191	1.191	1.192	1.196	1.194	1.199
NN	1.303	1.423	1.433	1.288	1.304	1.305	1.299	1.292	1.299	1.287
NC_{anti}	1.457	1.479	1.479	1.450	1.464	1.458	1.471	1.457	1.476	1.455
NC_{syn}	1.458	1.479	1.479	1.451	1.457	1.466	1.462	1.474	1.461	1.474
∠NCN	95.7	89.6	90.2	97.0	96.1	96.4	95.6	95.5	96.2	97.0
∠NNo	114.6	112.6	114.1	114.6	114.7	114.8	114.5	115.6	115.0	115.6
∠α[e]	26.5	58.3	50.2	0	28.0	28.9	26.0	15.7	24.7	10.0
∠β[e]	10.5	28.1	28.4	0	12.4	11.3	11.1	10.2	8.2	5.4
$\angle ONNC_{anti}$	157.1	130.6	52.6	180	156.0	155.2	158.3	166.8	158.3	171.1
$\angle ONNC_{syn}$	21.1	130.6	52.6	0	22.2	22.6	19.5	15.5	19.4	8.6
μ	4.434	3.140	2.630	4.780	4.371	4.239	4.330	4.395	4.291	4.360
E_{rel}	0.0	17.92	20.60	0.33	0.0	0.28	0.0	0.72	0.0	1.00
E_{rel}(incl ZPVE)	0.0	17.47	20.12	0.17	0.0	0.31	0.0	0.74		

[a] Bond lengths in angstroms, angles in degrees. [b] In Debye. [c] In kilocalories per mole. [d] Conformation as depicted in Scheme 3 (R = Me). [e] See Figure 1.

Scheme 3



Scheme 4



the maximal $n_N-\pi^*_{NO}$ conjugation, which leads to full flattening of the ring as well ($\alpha = \beta = 0°$), is realized in the planar fragment, NNO, of TS_{inv}-**1**. Analogously, *N*-nitrosoazetidine *Z*-**4**, having the lowest pyramidality of the ring nitrogen atom in the series of the ground states of **1**–**4** (Table 1), is characterized by the most flattened ring ($\beta = 5.4°$).

The presence of the methyl group removes the degeneracy of the equilibrium between the +*sc*- and −*sc*-rotamers of *N*-nitrosoazetidine **2** (Scheme 3, Table 1). Destabilization of the *Z*-(+*sc*)-rotamer of **2** is mainly caused by the steric interactions between the nitroso and methyl groups. The same situation applies in principle to the *E*,*Z*-rotamers of trialkylazetidines **3** and **4** (Scheme 3). However, the steric repulsion of the nitroso group and the *cis*-pseudoaxial 2-alkyl group in the *Z*-isomer is more importnat for these compounds. Unlike *N*-nitrosoaziridines,[2g] the $\sigma_{CN}-\pi^*_{NO}$ and $n_N-\sigma^*_{CN}$ orbital interactions probably do not have much influence on the *Z*,*E*-isomerization of *N*-nitrosoazetidines **2**–**5** because the azetidine ring has a smaller donor–acceptor capacity of the CN bonds than does the aziridine ring. The decrease of the ring nitrogen pyramidality, firstly, reduces the bonding CN orbital energies and raises the antibonding σ^*_{Cn} and π^*_{NO} orbital energies and, secondly, strongly diminishes σ_{CN} and π^*_{NO} orbital overlapping but influences to a lesser degree the energy of the n_{NO} orbital and the overlapping of the latter with the σ^*_{CN} orbital. In 2-methylazetidine **2**, the C(4)–N bond is a better acceptor than the C(2)–N bond and $n_{NO}-\sigma^*_{CN}$ interactions (Scheme 4) make a contribution in an increase of the polarity of *E*-**2** in the comparison with the *Z*-**2** isomer, which has the relatively unfavorable *cis* orientation of the C(4)–N bond and the n_{NO} orbital (Scheme 4). In azetidines **3** and **4**, the C(4)–N bond is a better acceptor, and one also expects a greater polarity of the *E*-isomer for these compounds. However, the $n_N-\pi^*_{NO}$ conjugation is the dominting factor in the case of **3** and **4** because their *Z*,*E*-isomers differ significantly due to the degree of ring nitrogen pyramidality (Table 1). Therefore, the *Z*-isomer with the more planar nitrogen atom is more polar in the *Z*,*E*-pairs of **3** and **4**. Opposite contributions of the $n_{NO}-\sigma^*_{CN}$ and $n_N-\pi^*_{NO}$ interactions in the polarity of the *Z*,*E*-isomers of **3** and **4** lead to a reduction of the difference of the dipole moments for these isomers in comparison with the difference for the *Z*,*E*-isomers of **2** (Table 1).

The calculated data, which predict a preference for the *E*-isomers of **2**–**4**, are in good agreement with the experimental results of the ^{1}H NMR studies of **2** and **5**. The *Z*,*E*-isomers of these compounds are observed on the signals of the monomethyl group and the ring α-protons (Table 2). It is known that the nitrosoamino group exerts a shielding influence on the protons that are *cis*-oriented in respect to the oxygen atom of this group.[11] Hence, the predominant isomer of *N*-nitrosoazetidine **2**, having the upfield shift of the α-methylene protons, has been assigned to the *E*-isomer, and the minor isomer with the more shielded α-methine proton and the Me group has been assigned to the Z-isomer. The assignment for *N*-nitrosoazetidine **5** has been made similarly. In the predominant isomer *E*-**5**, the α-methine proton and the Me group are in the *cis*-position to the oxygen atom, and correspondingly, their signals have more upfield shifts in comparison with these signals for minor *Z*-**5** (Table 2).

A greater value of an aromatic solvent-induced shift (ASIS effect) for the *trans*-α-proton[11] and a greater difference in chemical shifts of the geminal protons of the *cis*-α-CH_2 group[11b] are other criteria for the assignment of the *Z*,*E*-isomers of *N*-nitrosoazetidines. Application of these criteria in the case of *N*-nitrosoazetidine **2** confirms the above assignment. Indeed, the greater ASIS effect for the α-methine proton and the geminal nonequivalence of the protons of the α-CH_2 group are observed for the major isomer *E*-**2**, whereas a greater ASIS effect for α-methylene protons and the equivalence of the protons of this group are inherent for minor isomer *Z*-**2** (Table 2).

The small but discernible increase of population of the major *E*-isomer in the *Z*,*E*-pair of **2** and of the minor *Z*-isomer in the *Z*,*E*-pair of **5** with an increase of the solvent polarity (Table 2) is consistent with the greater polarity of these conformers.

Table 2. Selected ^{1}H NMR Data[a] and the Equilibrium Content[b] of the *Z*,*E*-Isomers of *N*-nitrosoazetidines **2** and **5**

compd	solvent	δ (ASIS effect)[c] α-CH	α-CH_2	*Me*CH	equilibrium content
E-**2**	cyclohexane-d_{12}	5.05	3.84, 3.92	1.63	74
	C_6D_6	4.39	3.48, 3.56	1.12	76
	$CDCl_3$	5.22 (0.83)	4.09 (0.61), 4.20 (0.64)	1.74 (0.62)	79
	CD_3OD	5.21	4.08, 4.19	1.68	79
Z-**2**	cyclohexane-d_{12}	4.49	4.59	1.35	26
	C_6D_6	4.16	3.91	1.05	24
	$CDCl_3$	4.75 (0.59)	4.78 (0.87)	1.49 (0.45)	21
	CD_3OD	4.73	4.77	1.45	21
E-**5**	cyclohexane-d_{12}	4.30		1.34	80
	$CDCl_3$	4.53		1.48	79
	CD_3OD	4.54		1.44	73
Z-**5**	cyclohexane-d_{12}	4.75		1.60	20
	$CDCl_3$	4.87		1.67	21
	CD_3OD	4.89		1.63	27

[a] Chemical shifts of ^{1}H in parts per million. [b] In percent. [c] $\delta_{CDCl3} - \delta_{C_6D_6}$.

Table 3. CD and UV Spectra[a] of *N*-Nitrosoazetidines **2** and **5**

compd	spectra	solvent	band I (n−π*)	band II (π−π*)
2	CD	heptane	386 (0.696), 372 (0.665)	238 (−1.38)
		MeCN	364 (0.744)	236 (−1.47)
		MeOH	350 (0.728)	235 (−1.75)
	UV	heptane	388 (96), 375 (99)	238 (7600)
		MeOH	351 (85)	235 (8600)
5	CD	heptane	402 (0.719), 359 (−0.222)	239 (−3.76)
		MeCN	393 (0.343), 358 (−0.461)	248 (−1.19), 216 (0.49)
		MeOH	391 (0.152), 346 (−0.614)	252 (−0.49), 220 (0.79)
	UV	heptane	393 (77), 379 (83)	239 (5670)
		MeOH	357 (83)	238 (6920)

[a] Wavelengths of apparent maxima in nanometers, $\Delta\epsilon$ and ϵ values in parentheses.

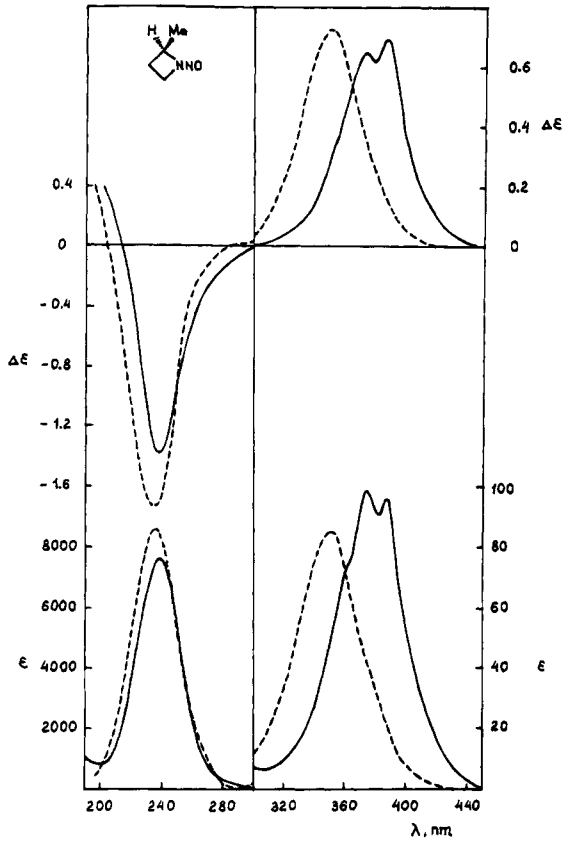


Figure 2. CD and UV spectra of *N*-nitrosoazetidine **2** in heptane (—) and MeOH (- - -).

The pseudoaxial orientation of the α-methine proton and, correspondingly, the pseudoequatorial orientation of the methyl group in *N*-nitrosoazetidines **2** and **5** follow from the values of the vicinal coupling constants of this proton: 6.4 and 7.2 Hz for *E*-**2**, 6.1 and 7.5 Hz for *Z*-**2**; 6.2 and 8.7 Hz for *E*-**5**, and 6.5 and 8.7 Hz for *Z*-**5**. As was shown earlier,[10a] one of the constants ^3J would be less than 5.1 Hz (pseudoequatorial−pseudoequatorial spin coupling) in the case of a pseudoequatorial orientation of this proton.

Thus, for examination of the chiroptical properties of *N*-nitrosoazetidines **2** and **5**, one can assume simple two-position equilibria, in the first instance, between the *Z*,*E*-isomers with the pseudoequatorial orientations of the nitroso and methyl groups (Scheme 3). The interpretation of the CD spectrum of **5**, however, may be complicated by the fact that the analysis

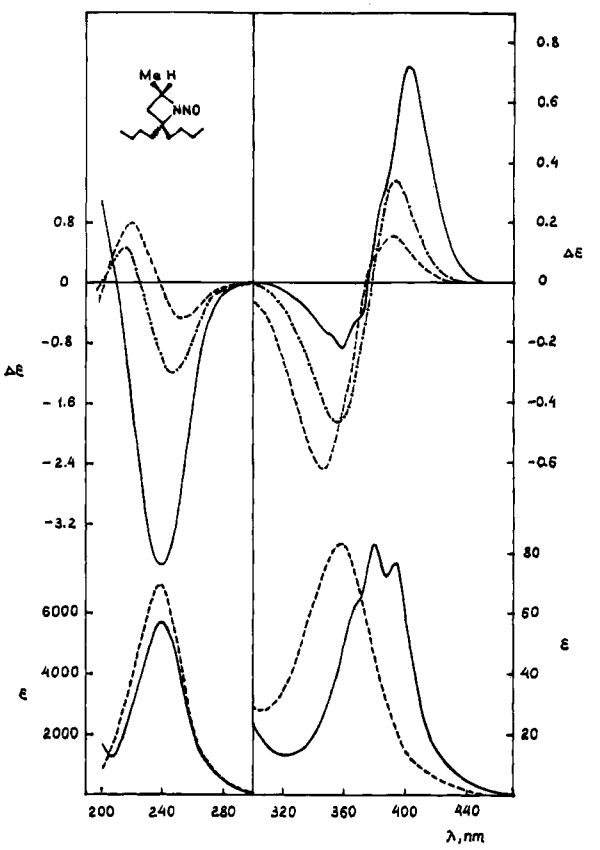


Figure 3. CD and UV spectra of *N*-nitrosoazetidine **5** in heptane (—), MeOH (- - -), and MeCN (— • —).

must take into account possible conformational complexity due to the *n*-butyl gorups, which will not be averaged out as it was in the NMR experiment.

Chiroptics. As in the cases of other *N*-nitrosoamines,[2] the CD and UV spectra of *N*-nitrosoazetidines **2** and **5** contain two main absorption bands, one in the region of 380 nm (band I) and the other at 240 nm (band II) (Table 3, Figures 2 and 3). The difference in wavelengths of these bands (140 nm) is well-reproduced by the calculations of the lowest excited singlet states of *N*-nitrosoazetidines **1**−**4** (Table 4).

Examination of MO's participating in two first electronic transitions (Figure 4) reveals that *N*-nitrosoazetidines have the same orbital origin of these transitions as virtually planar *N*-nitrosoamines[12] and nonplanar *N*-nitrosoaziridines,[2f,g] i.e. band I is caused by the n−π* transition and band II by the π−π* one. The experimental values of the extinction coefficients (ϵ) in the UV spectra of *N*-nitrosoazetidines **2** and **5** (Table 3) and the calculated oscillator strengths (Table 4) indicate a "forbidden" character of the first electronic transition and an "allowed" character of the second one and confirm the assignment.

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Table 4. Calculated Electronic Properties for *N*-Nitrosoazetidines **1**–**4**[a]

property	−*sc*-**1**	*E*-(−*sc*)-**2**	*Z*-(+*sc*)-**2**	*E*-(−*sc*)-**3**	*Z*-(+*sc*)-**3**	*E*-(−*sc*)-**4**	*Z*-(+*sc*)-**4**
			S_0–S_1 (n–π^*)				
E, eV	4.04	4.07 (3.72)	4.04	4.16	4.19	(3.77)	(3.87)
$[R]^r$	+8.38	+10.2 (+8.3)	−11.1	+11.5	−5.8	(+5.7)	(−4.3)
$[R]^\nabla$	+0.8	+0.6	−0.5	+3.9	−2.1		
f	0.004	0.005 (0.003)	0.006	0.005	0.005	(0.003)	(0.003)
			S_0–S_2 (π–π^*)				
E, eV	7.57	7.68 (7.27)	7.60	8.06	7.94	(7.26)	(7.17)
$[R]^r$	−51.2	−55.2 (−63.3)	+31.5	−37.4	−2.4	(−37.1)	(+30.3)
$[R]^\nabla$	−12.9	−13.0	+8.7	−31.4	−0.3		
f	0.1543	0.168 (0.321)	0.144	0.249	0.216	(0.315)	(0.296)

[a] With PCI. Values shown in parentheses were derived with G92(CIS), see Computational Methods for explanation.

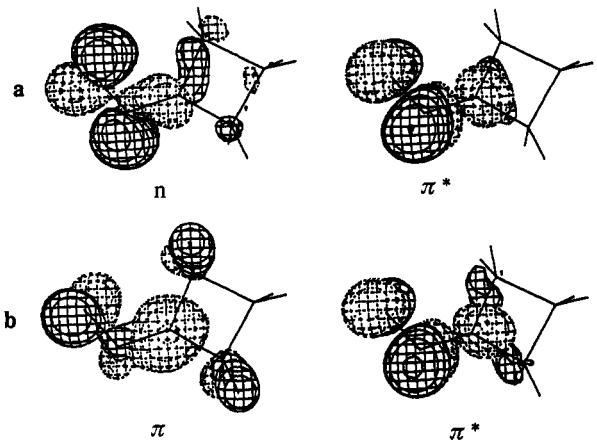

Figure 4. Singly occupied molecular orbitals of the two lowest excited states of 1-nitrosoazetidine (**1**): (a) first excited state (n–π^*). (b) second excited state (π–π^*).

Earlier,[2f,g] it was shown that a weakening of the n_N–π^*_{NO} conjugation at a deviation from planarity of the nitrosamine chromophore leads to a bathochromic shift of band I. This shift is mainly caused by a decrease of the terminal π^*_{NO} orbital energy and reaches ~100 nm for high-pyramidal *N*-nitrosoaziridines in comparison with virtually planar *N*-nitrosoamines. The nitrosoazetidine chromophore has a small deviation from the planarity and, correspondingly, a small reduction of the π^*_{NO} orbital energy. An effect from the latter can be counteracted by a reduction of the initial n_{NO} orbital energy, owing to the n_{NO}–σ^*_{CN} interaction (Scheme 4, admixture of the σ orbital of the *syn*-CN bond to the n_{NO} orbital, as is evident in Figure 4a). Therefore, the wavelength of band I in the CD and UV spectra of *N*-nitrosoazetidine **2** practically coincides with the wavelength of band I for the closest analogue, 1-nitroso-2-methylpyrrolidine,[2d] which no doubt has the more planar chromophore.

The calculated rotational strengths of the n–π^* transition as well as the π–π^* one for *Z*,*E*-isomers of *N*-nitrosoazetidine **2** have similar values and opposite signs (Table 4). Therefore, the greater population of the *E*-(−*sc*)-isomer with the positive sign of the rotational strength of the n–π^* transition and the negative sign of the π–π^* one provides the observed CE signs in the CD spectra of this compound (Figure 2, Table 3). Some increase of the intensity of both CEs with the increase of the polarity and proton donor capacity of a solvent reflects the shift of the equilibrium toward the more polar *E*-(-*sc*)-isomer. The ratio of the first and second CE intensities (Table 3) also is reproduced qualitatively and correctly by the calculations (Table 4).

Bands I and II in the CD spectra of *N*-nitrosoazetidine **5**, unlike those of *N*-nitrosoazetidine **2**, have a bisignate form (Figure 3, Table 3). A similar form of band I was earlier observed in the CD spectra of some *N*-nitrosopyrrolidines[2d,e] and was explained[2d] by contributions of the allowed (due to molecular chirality) and forbidden (due to molecular vibration) components with the opposite signs in this band. According to a recent postulate,[2e] the bisignate form may be caused by the equilibrium between two half-chair (twisted) conformations of the pyrrolidine ring.

The separate contributions of the allowed and forbidden components of dichoric absorption are usually observed for bands with strong vibronic structure,[2d,e] whereas band I of *N*-nitrosoazetidine **5** has practically no such structure even in a nonpolar solvent (Figure 3). Besides, unlike the pyrrolidine ring, the azetidine ring cannot have chiral conformations. Consequently, it can be supposed that the form of band I in the CD spectra of *N*-nitrosoazetidine **5** is caused by contributions of the *Z*,*E*-isomers (Scheme 3). The decrease of the long-wavelength component intensity and the increase of the short-wavelength one in polar solvents (Figure 3, Table 3) allow the assignment of the long wavelength component to a contribution of the less polar (−*sc*)-isomer, *E*-**5**, and the short-wavelength component to the more polar *Z*-(+*sc*)-isomer. Such assignment is in agreement with the calculation results of model *N*-nitrosoazetidines **3** and **4**. According to these calculations, *E*-(−*sc*)-**3** and **4** are characterized by the smaller energy and the positive rotational strength of the n–π^* transition and the *Z*-(+*sc*)-isomers by the greater energy and the negative rotational strength of this transition (Table 4).

The calculated difference in the n–π^* transition energies for the *Z*,*E*-isomers of *N*-nitrosoazetidine **3** (0.03 eV, $\Delta\lambda$ = 2 nm) is the same as in the case of the *Z*,*E*-isomers of **2**. With such a small difference, one would not expect to see the separate transitions, and this is in accord with the experimental CD spectra of **2** in which band I is not bisignate (Figure 2). However, for the *Z*,*E*-isomers of **4**, which is a better model of 2,2-dibutyl-substituted **5**, this difference is predicted to be more considerable and reaches 0.1 eV ($\Delta\lambda$ = 9 nm). The calculations are in the absence of solvent. Since the spatial environment of the nitroso group in the *Z*,*E*-isomers is different to a much greater degree for **5** than for **2**, it is possible that differential solvation of the nitroso group may further increase the difference in the n–π^* transition wavelength for *Z*,*E*-isomers of **5**, whereas for *Z*,*E*-**2**, solvation of this group should be almost identical. Whether solvation has this effect or not, the computed wavelength difference for the oppositely signed transitions is not

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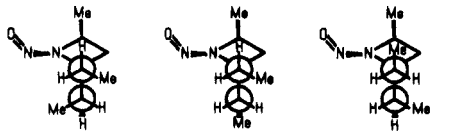
Scheme 5



	E-(-*sc*)-**4a**	*E*-(-*sc*)-**4c**	*E*-(-*sc*)-**4c**
ΔE, kcal mol^{-1} relative to *E*-**4** (Table 1, Scheme 3)	0.62	0.65	0.74
$[R]_{01}$	+9.0	+7.5	+8.3
$[R]_{02}$	-40.4	-20.4	-41.1

incompatible with the observed bisignate character of this transition in **5** since extensive cancellation of broad oppositely signed CEs will result in an observed peak to trough difference larger than the actual difference.

It should be noted, however, that there is a greater change of the relative intensities of the band I components with a change in the solvent polarity than would be expected from the experimental ratios of *Z,E* isomers **5** (Table 2) or from the calculated values of the optical rotational strengths of the n−π^* transition for the *Z,E*-isomers of model compounds **3** and **4** (Table 4).

The bisignate form of band II in the CD spectra of *N*-nitrosoazetidine **5** in polar solvents (MeCN and MeOH) (Figure 3, Table 3) can also be connected with an increasing population of the more polar *Z*-(+*sc*)-isomer, which must have the positive CE of the $\pi-\pi^*$ transition if this interpretation is correct. In fact, the calculation of the closest model, i.e. 2,2-diethyl-substituted azetidine (**4**), does predict the positive sign of the $\pi-\pi^*$ transition rotational strength for the *Z*-(+*sc*)-isomer and the negative sign for the *E*-(−*sc*)-isomer (Table 4). The observed longer wavelength position of the negative band II of the *E*-(−*sc*)-isomer of **5** in comparison with the position of positive band II for *Z*-(+*sc*)-**5** is evidently caused by a better solvation of the less sterically hindered nitroso group in *E*-(−*sc*)-**5**. At the same time, the calculated signs of the $\pi-\pi^*$ transition rotational strength of another model, i.e. 2,2-dimethyl-substituted azetidine **3**, are negative for both the *Z*-(+*sc*)- and the *E*-(−*sc*)-isomers. As one can see from Table 4, the chiroptical properties connected with this transition are more sensitive to a pertubative influence of ring substituents than properties connected with n−π^* transition. Moreover, the rotational isomerism of long-chained 2-alkyl substituents, such as ethyl or butyl groups, can be an additional source of perturbtion of not only the $\pi-\pi^*$ transition but also the n−π^* transition in the nitrosoazetidines chromophore because rotation around one $C_{ring}-CH_2R$ bond at least can lead to chiral rotamers. We have calculated the rotational strengths of the electronic transitions for several other rotamers of 2,2-diethylazetidine *E*-(−*sc*)-**4** (see Scheme 3 for structure), i.e. *E*-**4a**, *E*-**4b**, and *E*-**4c**, which are the next lowest energy structures on the potential energy surface of rotation about the C(2)−CH_2Me bond. These are shown in Scheme 5. The calculated results indicate that the conformational isomerism of 2-alkyl substituents has a greater influence on the $\pi-\pi^*$ transition rotational strength than on the n−π^* one. However, for both of the transitions, this influence is only expressed as changes in the rotational strength values, whereas the signs remain invariable. Thus, it is evident that the CE sign of the n−π^* transition is the more reliable criterion for the examination of the absolute stereochemistry of *N*-nitrosoazetidines. This sign is undoubtedly connected with the intrinsic chirality of the nitrosoazetidine chromophore, and as it is shown above, the chirality is determined by the closest spatial environment of the chromophore. All −*sc*-rotamers of *N*-nitrosoazetidines **1**−**5** have the positive CE sign of the n−π^* transition and vice versa. This is in full agreement with a spiral rule established earlier[2f,g] for other nonplanar nitrosoamines, *N*-nitrosoaziridines, whereas absence of the local plane of symmetry in the nitrosoazetidine chromophore does not permit the use of well-known sector rules.[2a-e]

Conclusions

The introduction of the tricoordinated nitrogen atom of the nitrosoamino group into the four-membered ring weakens the $n_N-\pi^*_{NO}$ conjugation and provides the pyramidal configuration of this atom in the ground state. Thus, *N*-nitrosoazetidines possess the nonplanar intrinsically chiral nitrosoamine chromophore. The mechanism of the inversion of the chirality of this chromophore for the parent *N*-nitrosoazetidine is similar to the mechanism for the parent *N*-nitrosoaziridine.[2g] However, the deviation from the planarity of the chromophore and, correspondingly, a weakening of the $n_N-\pi^*_{NO}$ conjugation are relatively small. Therefore, on some parameters (barriers of rotation about the NN bond, wavelengths of the n−π^* transition), *N*-nitrosoazetidines are found nearer to virtually planar *N*-nitrosoamines than to high-pyramidal *N*-nitrosoaziridines. Nevertheless, the CE sign of the n−π^* transition in the CD spectra of *N*-nitrosoazetidines is only determined by the intrinsic chirality of the chromophore and obeys a spiral rule;[2f,g] the left-spiral −*sc*-rotamers are characterized by the positive CE sign and the right spiral +*sc*-rotamers by the negative one.

The equilibrium population of the +*sc*- and −*sc*-rotamers is controlled by the steric interaction between the nitroso group and the azetidine ring substituents. Hence, the CE sign of the n−π^* transition can be connected with the absolute configurtion of chiral centers in the molecule. The problem is simplified because the nitroso group in *N*-nitrosoazetidines always prefers the pseudoequatorial orientation, and the *Z,E*-isomers ratio can be determined from the ^{1}H NMR spectra.

Computational Methods

The structures of nitrosoazetidines **1**−**4** were fully optimized at the Hartree−Fock level using procedures implemented in the Gaussian 92 system of programs and the internal 6-31G* basis set. Compound **1** has one minimum energy structure, compounds **2** and **3** have two, while compound **4** has 18. The transition structures for pyramidal inversion at N and for rotation about the NN bond of **1** were located. Harmonic frequency analysis verified the nature of the stationary points as minima (all real frequencies) or as transition structures (one imaginary frequency) and was used to provide an estimate of the zero-point vibrational energies (ZPVE) of **1**−**3**. Relative energies were estimated at the HF/6-31G* or HF/6-31+G* level with ZPVE corrections, except for **4**. For the purpose of Boltzmann population analyses, 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 diffuse s and p functions designated by the "+" is desired for a more accurate description of the excited singlet state. 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 state and the 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 determinant wave function. 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 **1** and **2** may be for larger molecules like **3** and **4**. PCI has been extensively used,[13-16]

and the theory is described in detail elsewhere.[17] On the other hand, a CIS calculation, as implemented in the Gaussian 92 package[18] (G92/CIS), uses a window of all valence-occupied and -unoccupied orbitals but does not include the ground state correlation contribution. For all of the conformers of **4** that have significant populations at 298 K, rotatory strengths were calculated by G92/CIS.[18] Molecular orbitals of the excited states are displayed as mdified Jorgensen−Salem plots.[19]

Experimental Section

The CD spectra were measured on a JASCO J-500A spectropolarimeter with a DP-500N data processor, the UV spectra on a Specord UV−vis spectrophotometer, the ^{1}H NMR spectra on a Bruker ACE-200 spectrometer (200 MHz, from TMS), and the optical rotation angles on an Autopol III polarimeter.

(1-1′-Phenylethyl)-4-methylazetidin-2-one (7). Thionyl chloride (14.3 g, 120 mmol) was added dropwise to diastereomerically pure *N*-(1′-phenylethyl)-3-aminobutyric acid[5] (6.22 g, 30 mmol) and DMF (0.1 g) in absolute CH_2Cl_2 (70 mL) with stirring, and the stirring was continued for 48 h at 25 °C. After the removal of the solvent and the excess of $SOCl_2$ in vacuo, the solid residue was dissolved in absolute CH_2Cl_2 (250 mL), and the obtained solution was added dropwise to a boiling solution of Et_3N (12.14 g, 120 mmol) in absolute CH_2Cl_2 (150 mL). The refluxing was continued for 0.5 h, and the cooled reaction mixture was washed with water (2 × 30 mL) and dried over $MgSO_4$. The solvent was evaporated in vacuo, and the product was extracted from the residue with hexane. After the removal of hexane in vacuo, the oil residue was distilled, providing azetidinone **7**.

(1′*S*,4*R*)-7: yield 87%; bp 101−102 °C (0.2 mm); $[\alpha]^{25}_D$ −29.0° (*c* 1.7, $CHCl_3$); ^{1}H NMR in $CDCl_3$ (*J*, Hz) δ 1.09 (d, 4-Me, ^3J = 6.2), 1.71 (d, *Me*CHN, ^3J = 7.0), 2.46 (dd, 3-H, ^2J = −14.4, ^3J = 2.1), 3.01 (dd, 3-H, ^2J = −14.4, ^3J = 5.0), 3.59 (m, 4-H), 4.67 (q, C*H*N), 7.22−7.45 (m, Ph).

(1′*S*,4*S*)-7: yield 91%; bp 96−98 °C (0.2 mm); $[\alpha]^{25}_D$ −61.9° (*c* 1.5, $CHCl_3$); $[\alpha]^{25}_D$ −38.1° (*c* 1.3, CH_2Cl_2) {lit.[7b] bp 111−112 °C (0.2 mm); $[\alpha]^{20}_D$ −36° (*c* 1.2, CH_2Cl_2)}; ^{1}H NMR in $CDCl_3$ (*J*, Hz) δ 1.26 (d, 4-Me, ^3J = 6.1), 1.64 (d, *Me*CHN, ^3J = 7.2), 2.46 (dd, 3-H, ^2J = −14.4, ^3J = 2.4), 2.98 (dd, 3-H, ^2J = −14.4, ^3J = 5.1), 3.52 (m, 4-H), 4.92 (q, C*H*N), 7.26−7.42 (m, Ph).

4-Methylazetidin-2-one (8). Small pieces of sodium metal (2.3 g, 100 mmol) were added to a solution of diastereomerically pure azetidinone **7** (4.73 g, 25 mmol) in liquid ammonia (200 mL) with stirring and cooling (−40 °C), and the stirring was continued for 2 h at the same temperature. After the addition of solid NH_4Cl (6 g) and the removal of ammonia, the product was extracted from the residue with CH_2Cl_2, and then the extract was evaporated in vacuo. The residue was distilled, providing azetidinone **8**: bp 69−70 °C (0.2 mm) {lit.[20] bp 50 °C (0.1 mm)}; ^{1}H NMR in $CDCl_3$ (*J*, Hz) δ 1.36 (d, Me, ^3J = 6.1), 2.54 (m, 3-H, ^2J = −14.7, ^3J = 2.3, ^4J = 1.4), 3.1 (m, 3-H, ^2J = −14.7, ^3J = 4.9, ^4J = 2.0), 3.77 (m, 2-H), 6.2 (br s, NH).

(4*R*)-8: yield 80%; $[\alpha]^{25}_D$ +3.6° (*c* 2.3, $CHCl_3$).

(4*S*)-8: yield 85% $[\alpha]^{25}_D$ −3.7° (*c* 2.4, $CHCl_3$).

(2*R*)-1-Nitroso-2-methylazetidine (2). A solution of azetidinone (4*R*)-**8** (1.62 g, 19 mmol) in absolute ether (20 mL) was added dropwise to $LiAlH_4$ (3.6 g, 95 mmol) in absolute ether (100 mL) with stirring, and the reaction mixture was refluxed for 4 h. After decomposition of the reaction mixture with 4.7% aqueous NaOH (13.5 mL) at 0−5 °C, the white precipitate was filtered off. A part of the product was steam-distilled from the precipitate. The distillate (40 mL) was acidified with concentrated HCl (12 mL), and the resulting solution was used for washing the ether solution. Small portions of $NaNO_2$ (13.11 g, 190 mmol) were added to the acidic solution (52 mL) and CH_2Cl_2 (20 mL) with stirring, and the stirring was continued for 10 h at 25 °C. After the separation of the organic layer, the aqueous solution was extracted with CH_2Cl_2 (3 × 10 mL). The combined extract was dried over $CaCl_2$ and evaporated in vacuo. The residue was distilled, providing *N*-nitrosoazetidine **2** (1.12 g, 59%): bp 43−44 °C (0.25 mm); $[\alpha]^{25}_D$ +22.1° (*c* 1.8, $CHCl_3$); ^{1}H NMR in $CDCl_3$ (*J*, Hz) δ 1.49 (d, Me^Z, ^3J = 6.5), 1.74 (d, Me^E, ^3J = 6.5), 1.92−2.10 (m, 3-H_a^{E+Z}), 2.47−2.65 (m, 3-H_e^{E+Z}), 4.09 (m, 4-H_a^E), 4.20 (m, 4-H_e^E), 4.75 (m, 2-H_a^Z, ^3J = 6.1, 6.5, 7.5, ^4J = 1.5), 4.78 (dt, 4-$H_aH_e^Z$, ^4J = 1.5), 5.22 (m, 2-H_a^E, ^3J = 6.4, 6.5, 7.2 ^4J = 0.8, 1.9). Anal. Found: C, 48.4; H, 8.3; N, 27.6. Calcd for $C_4H_8N_2O$: C, 48.0; H, 8.1; N, 28.0.

(4*S*)-2,2-Dibutyl-4-methylazetidine (10). A solution of azetidinone (4*S*)-**8** (1.45 g, 17 mmol) in absolute CH_2Cl_2 (10 mL) was added to a solution of $Et_3O^+BF_4^-$ (3.23 g, 17 mmol) in absolute CH_2Cl_2 (20 mL) with stirring. After 5 h at 25 °C and 0.5 h at 40 °C, the solvent was removed in vacuo, and absolute ether (50 mL) was added to the residue. A 10 M hexane solution of *n*-butyllithium (10.2 mL, 102 mmol) was added dropwise via a syringe to the resulting mixture with cooling (−40 °C) and stirring under nitrogen. The stirring was continued for 24 h at −20 °C, and the reaction mixture was carefully decomposed with water (50 mL). After the separation of the organic layer, the aqueous solution was extracted with ether (3 × 30 mL), and the combined extract was washed with cooled (0 °C) 2 N aqueous H_2SO_4 (3 × 15 mL). The resulting acidic solution was basified with 40% aqueous KOH, saturated with KOH pellets, and extracted with ether (5 × 15 mL). The combined ether extract was dried over K_2CO_3 and evaporated in vacuo. The residue was distilled, providing azetidine **10** (1.74 g, 56%): bp 55−56 °C (0.25 mm); $[\alpha]^{25}_D$ + 5.0° (*c* 1.7, heptane); ^{1}H NMR in $CDCl_3$ (*J* Hz) δ 0.92 (dt, *Me*CH2, ^3J = 6.7, 7.2), 1.06−1.63 (m, CH_2CH_2-CH_2), 1.21 (d, *Me*CH, ^3J = 6.2), 1.61 (dd, 3-H, ^2J = −11.0, ^3J = 7.6), 1.84 (br s, NH), 2.08 (dd, 3-H, ^2J = −11.0, ^3J = 8.0), 3.76 (m, 4-H). Anal. Found: N, 7.3. Calcd for $C_{12}H_{25}N$: N, 7.6.

(4*S*)-1-Nitroso-2,2-dibutyl-4-methylazetidine (5). To a solution of azetidine (4*S*)-**10** (0.733 g, 4 mmol) in CH_2Cl_2 (10 mL) was added 10.5% aqueous HCl (13.2 mL) dropwise with stirring and cooling (0 °C). Small portions of $NaNO_2$ (2.76 g, 40 mmol) were added to the resulting mixture, and the stirring was continued for 10 h at 25 °C. After the separation of the organic layer, the aqueous solution was extracted with CH_2Cl_2 (3 × 20 mL), and the combined extract was dried over $CaCl_2$ and evaporated in vacuo. Flash chromatography (silica gel 60, 230−400 mesh, EtOAc−petroleum ether, 1:9) gave *N*-nitrosoazetidine **5** (0.752 g, 88.5%): $[\alpha]^{25}_D$ +27.9° (*c* 1.7, $CHCl_3$); ^{1}H NMR in $CDCl_3$ (*J*, Hz) δ 0.93 (m, $MeCH_2^{E+Z}$, ^3J = 6.6, 7.0), 1.23−1.53 (m, $CH_2CH_2^{E+Z}$), 1.48 (d, $MeCH^E$, ^3J = 6.6), 1.67 (d, $MeCH^Z$, ^3J = 6.5), 1.78 (dd, 3-H_a^E, ^2J = −11.2, ^3J = 6.2), 1.82 (dd, 3-H_a^Z, ^2J = −11.1, ^3J = 6.5), 1.87−2.05 (m, CH_2C^{E+Z}), 2.25 (dd, 3-H_e^Z, ^2J = −11.1, ^3J = 8.7), 2.31 (dd, 3-H_e^E, ^2J = −11.2, ^3J = 8.7), 4.53 (m, 4-H_a^E), 4.87 (m, 4-H_a^Z). Anal. Found: C, 68.2; H, 11.5; N, 13.1. Calcd for $C_{12}H_{24}N_2O$: C, 67.9; H, 11.4 N, 13.2.

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