Structure, Conformation, and Stereodynamics of *N*-Nitroso-2,4-diaryl-3-azabicyclo[3.3.1]nonanes and *N*-Nitroso-2,4-diaryl-3-azabicyclo[3.3.1]nonan-9-ones[1]

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Received January 2, 1996[⊗]

The variable temperature ^{1}H, ^{13}C, and ^{19}F NMR spectra were measured for the title *N*-nitrosamines. The observed unusually low N−N rotation barriers (12−15 kcal/mol) result from a significant deviation of the nitrosamino system from planarity. A pyramidal character of the amino nitrogen was confirmed by the X-ray crystal structures of two compounds and by bathochromic shifts of the n−π* absorption bands in the UV spectra. The nonplanarity of the nitrosamino moiety is due to the strong pseudoallylic A$^{(1,3)}$ strain caused by the steric interaction of the NNO group with the neighboring aryl substituents fixed in the equatorial positions of the bicyclic skeleton. In addition, the barriers to the C−C rotation of aryl groups were examined at temperatures lower than required to "freeze" the N−N rotation and different $\Delta G^{\ddagger}$ values were observed for the aryls oriented *syn* and *anti* to the nitroso oxygen.

Introduction

The conformational properties of *N*-nitrosamines are a subject of continuing interest and research efforts because of their biological activity as potential carcinogens.[2] The partial double bond character between the adjacent nitrogen atoms brought about by the polar resonance structure of the type $>N^+=N-O^-$ leads to the restricted rotation about the N−N bond.[3] Variable temperature NMR spectroscopy allows the determination of the activation parameters of this process. Since the N−N rotation is slow on the NMR time scale the magnetically nonequivalent atoms oriented *syn* and *anti* to the nitroso oxygen can be detected in either ^{1}H or ^{13}C NMR at room temperature.[4] However, the corresponding resonances coalesce, when higher temperatures are attained. The N−N rotational barriers have been reported for a number of *N*-nitrosamines.[3] They are relatively high (ca. 23−25 kcal/mol)[3] for the planar nitrosamine systems due to the stabilizing interaction of the electron lone pair of the amino nitrogen with the π electrons of the NO group ($n_N-\pi_{NO}$* conjugation).[5] A weakening of the above $n_N-\pi_{NO}$* conjugation in nonplanar nitrosamine group results in the decreased N−N rotation barrier,[5,6] as it occurs in *N*-nitrosoaziridines characterized by a pyramidal configuration at the amino nitrogen.[5a,6]

The spectral properties of nonplanar nitrosamine systems are of special interest; however, compounds with the NNO group significantly deviated from planarity are rather rare. Besides, the small ring compounds, like *N*-nitrosoaziridines, are extremely unstable and rapidly decompose below room temperature.[7] Our recent study on *N*-nitroso-*cis*-2,6-diphenylpiperidines showed that the chair diequatorial conformation is destabilized by a strong allylic (pseudoallylic) A$^{(1,3)}$ strain[8] caused by a steric interaction of nearly coplanarly located bulky phenyl substituents with the NNO group.[9] To avoid this strain a molecule may force the substituents into the axial positions, assume a nonchair conformation, or increase a pyramidal character of the amino nitrogen driving the NO group out of the plane formed by the amino N-atom and α-substituents. We have chosen the title *N*-nitroso-2,4-diaryl-3-azabicyclo[3.3.1]nonanes and their 9-oxo derivatives because the aryl groups are fixed at the equatorial positions of the piperidine ring, being a part of a relatively rigid bicyclic skeleton,[10] and thus the A$^{(1,3)}$ strain cannot be relieved by the inversion or twisting of the ring but only by a distortion of the nitrosamino system from planarity. This expectation remains in line with the recently published X-ray structures of two compounds of this class.[11] In order to gather more information on the stereochemistry and consequences of the nonplanarity of the NNO group in these

[⊗] Abstract published in *Advance ACS Abstracts,* May 1, 1996.

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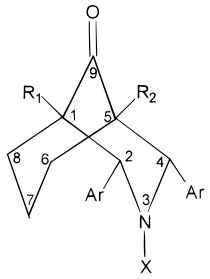
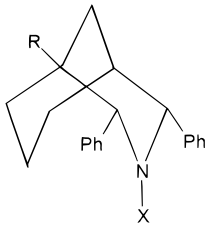
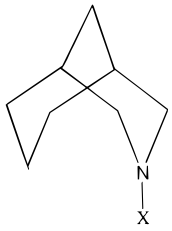
S0022-3263(96)00015-1 CCC: $12.00

easily accessible compounds we prepared derivatives **1b**−**10b** and studied their ^{1}H, ^{13}C, and ^{19}F NMR spectra. With use of the DNMR method we examined the influence of the molecular structure on the barriers to the N−N rotation and the hindered C−C rotation of the aryl substituents resulting from their interference with the NNO group. For comparison we prepared unsubstituted compound **11b**, which in absence of the A$^{(1,3)}$ strain, should exhibit properties characteristic for typical nitrosamines with the planar NNO system. The molecular geometries were studied by molecular mechanics (MM2) calculations,[12] the NMR spectroscopy, and the X-ray crystallographic analysis.





X=H	X=NO		X=H	X=NO
1a	**1b**	R_1=R_2=H, Ar=Ph	**9a**	**9b** R=H
2a	**2b**	R_1=H, R_2=Me, Ar=Ph	**10a**	**10b** R=Me
3a	**3b**	R_1=R_2=Me, Ar=Ph		
4a	**4b**	R_1=R_2=Me, Ar= 		
5a	**5b**	R_1=R_2=Me, Ar= 		
6a	**6b**	R_1=R_2=Me, Ar= 		
7a	**7b**	R_1=R_2=Me, Ar= 		
8a	**8b**	R_1=R_2=Me, Ar= 		



11a X=H

11b X=NO

Results and Discussion

2,4-*cis*-Diaryl-3-azabicyclo[3.3.1]nonan-9-ones **1a**−**10a** were prepared by a Mannich condensation of substituted benzaldehydes with appropriate cyclohexanones and ammonium acetate according to the literature methods.[13] 2,4-Diaryl-3-azabicyclo[3.3.1]nonanes were obtained by the Wolff−Kishner reduction of the corresponding ketones. The amine **11a** was synthesized by $LiAlH_4$ reduction of *cis*-cyclohexane-1,3-dicarboximide. The N-nitrosation of the amines with HNO_2 gave the *N*-nitrosamines **1b**−**11b**.

Molecular Geometry. *cis*-2,4-Diphenyl-3-azabicyclo-[3.3.1]nonan-9-one (**1a**) as well as the corresponding amine **9a** are known from crystallographic data to assume the chair−chair geometry of the bicyclic skeleton in the solid state.[14] A twin-chair conformation stabilized by phenyl substituents at equatorial positions is also evidenced by the ^{1}H and ^{13}C NMR spectra[15] and theoretical calculations.[16] Due to a spatial proximity of the N-3 and C-7 atoms in the above conformation the axial hydrogen at C-7 in amines **1a**−**10a** resonates at unusually low field (2.5−3.5 ppm), whereas the C-7 signal is observed at relatively high field (21−22 ppm). In the ^{13}C NMR of the corresponding nitrosamines **1b**−**10b** the shielding of the C-7 remains almost unaffected by N-nitrosation; however, deshielding effect of the N-3 in the ^{1}H NMR is somewhat weaker than in the parent amines, as shown by the chemical shift of the axial H-7 (1.6−2.6 ppm), presumably as a result of the changed hybridization of the nitrogen and the increased distance between the N-3 and C-7 atoms, due to flattening of the piperidine ring. Therefore the nitrosamines **1b**−**10b**, like their precursors **1a**−**10a**, must adopt a twin-chair conformation of the skeleton.[17] The reported X-ray structures of **9b**, the 4-methoxyphenyl analogue of **1b**,[11] and the crystal structures of 1,5-dimethyl derivatives **3b** and **8b** (Figure 1), solved by us,[18] confirm this supposition. They show the six-membered rings in the chair conformations flattened at the N-3 and C-7 atoms. A flattening of the piperidine ring is less pronounced in the 1,5-dimethyl derivatives **3b** and **8b** than in the compounds substituted with hydrogens at the C-1 and C-5 as shown by the distance of the N-3 from the plane defined by the C-1, C-2, C-4, and C-5 atoms: 0.38 and 0.44 Å for **3b** and **8b**, respectively (cf., the distance of 0.22 and 0.32 Å for **9b** and the analogue of **1b**, respectively). The energy minimum conformations calculated by the molecular mechanics (MM2) method[12] appeared to be very similar to those observed in the solid state. They are characterized by nearly perpendicular orientation of two aryl rings in respect to the plane defined by the C-1, C-2, C-4, and C-5 atoms of the piperidine ring, which minimizes their steric interaction with the skeleton atoms. In the case

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(17) Also in the case of the amine **11a** and nitrosamine **11b** the chair−chair conformation is preferred. This is confirmed by a relatively high field location of the C-7 signals in the ^{13}C NMR (at 23.1, 19.8, and 18.5 ppm in **11a**, its hydrochloride, and **11b**, respectively) and very weak vicinal coupling constants between H-1(5) and H-2(4) in the ^{1}H NMR spectra. The weaker deshielding of the axial H-7 (at 2.22 and 2.08 ppm in **11a** and **11b**, respectively) than in the corresponding 2,4-diaryl derivatives is probably due to a flattening of the piperidine ring.

(18) (a) The authors have deposited experimental details concerning the crystal structure determinations of **3b** and **8b**, atomic coordinates, anisotropic atomic displacement parameters of non-H atoms, and lists of bond lengths and angles with Cambridge Crystallographic Data Centre. The data can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K. (b) Two stereoisomers of **3b** differing in the orientation of the NNO group occupy, with equal probability, the same site in the crystal. In effect, a disordered structure with the carbonyl oxygen, C-7, C-9, N-3, and nitroso nitrogen atoms located on the statistical mirror plane arises. Even though the nitroso nitrogen atom does not show large anisotropic displacement parameters, the largest displacements are observed in the direction perpendicular to the symmetry plane and therefore one can expect that the N-atom is not exactly locatet on this plane but is slightly (ca. 0.1 A) shifted out from it. The above change of the nitrogen position would affect strongly the N−O distance and the NNO angle but only slightly influence the N−N distance. The disorder of the NNO group in *N*-nitrosopiperidines is rather a rule[9] than the exception and may be the source of the unusual geometrical parameters of the NNO moiety reported by Priya et al.[11b]

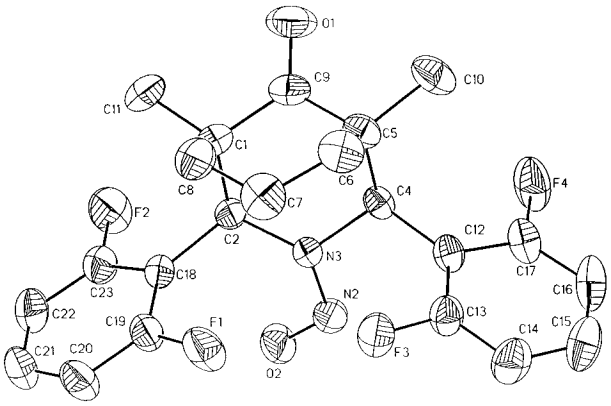

Figure 1. ORTEP drawing of the crystal structure of **8b**.

of monofluorophenyl compounds **6b** and **7b**, according to the MM2 method, there are four energy minima corresponding to four possible rotamers with different mutual orientations of the fluoroaryl rings and the nitroso group. However, owing to the strong dipole−dipole interactions between the 2-fluorophenyl moieties and steric repulsion between fluorine atoms and the NO group in **6b**, the contributions of two of them are negligible; the remaining two conformers of lower energies are shown in Figure 2. The population of the first one, with the fluorine atoms pointing outwards, is ca. 90%, as shown by the ^{19}F NMR spectrum at −50 °C (see supporting information). The second one of higher steric energy (by 0.7 kcal/mol) contributes much less (ca. 8%) to the conformational equilibrium. On the contrary, in the case of **7b** all four rotamers are nearly equally populated as indicated by the MM2 calculations and the low temperature ^{19}F NMR spectrum, which exhibits 8 fluorine signals of comparable intensity at −90 °C (Figure 3).

The important feature of the crystal structures of the title nitrosamines is a pyramidal character of the amino nitrogen as evidenced by a displacement of the N-3 atom from the plane formed by three neighboring atoms; it is more pronounced in the 1,5-dimethyl derivatives **3b** and **8b** (0.281 Å) than in the compounds bearing hydrogens at C-1 and C-5, i.e., the nitrosamine **9b** and the aforementioned analogue of **1b** (0.246 and 0.256 Å, respectively). The nonplanarity of the nitrosamine chromophore in solution is reflected by a bathochromic shift of the n−π* electronic transition in the UV spectra. The title compounds absorb at ca. 50 nm longer wavelengths than simple nitrosamines,[19] including **11b**, in hydrocarbon solvents. A notable property of the compounds **1b**−**10b** is their dark yellow color, which contrasts with pale yellow or colorless nitrosamines bearing the planar chromophore (e.g., **11b**). There are some subtle differences between the spectroscopic properties of the nitrosamines under study: compounds **3b**−**8b** with methyl groups at C-1 and C-5 absorb at longer wavelengths than the nitrosamine **1b** substituted with hydrogens at these positions, i.e., in the cyclohexane solution **3b** and **1b** show λ_{max} 417 (ϵ 85) and 410 nm (87), respectively. On the contrary, reduction of the carbonyl group shifts the absorbtion to shorter wavelengths, e.g., **9b** exhibits λ_{max} 405 nm (88) in cyclohexane. The above observations suggest that the degree of the chromophore distortion increases in the order: **9b** < **1b** < **3b**, in agreement with the X-ray data. The measured differences in the N−N rotation barriers also confirm the above sequence as will be discussed in the next section.

Dynamic NMR Spectra. The ^{1}H NMR spectra of nitrosamines **1b**−**10b** at room temperature show differentially broadened signals due to slowing conformational interconversion process. The ^{1}H NMR of the 9-oxo derivatives **1b**−**8b** exhibit only one average signal arising from the benzylic H-2 and H-4 protons. Similarly, the corresponding carbon atoms give rise to one broad resonance in the ^{13}C NMR. This indicates that the N−N rotation in the compounds under study is much faster than in typical nitrosamines at ambient temperatures. On lowering the temperature, decoalescence occurs and a pair of signals is observed for the atoms *syn* and *anti* to the NO group (Figures 4 and 5). The signals of the benzylic protons in **9b** and **10b** coalesce slightly above the room temperature indicating somewhat higher energy barriers to the N−N rotation in these compounds. In addition to ^{1}H or ^{13}C DNMR also variable temperature ^{19}F NMR spectra were measured for fluorophenyl compounds **5b**−**8b**. Because of their simplicity and large separation of the ^{19}F resonances (Figures 3 and 6) they appeared to be very useful for determination of energy barriers to rotation. The corresponding free energy of activation $\Delta G^{\ddagger}$ was calculated by substituting the coalescence temperature (T_c) and the chemical shift difference near the coalescence point ($\Delta\nu$) into the Eyring equation.[20] Unequal rotamer populations in the case of the unsymmetrically substituted compounds **2b** and **10b** require that the activation energy for the isomerization of the *Z* into the *E* form is different from the reverse process. In these cases the $\Delta G^{\ddagger}$ values were calculated using equations developed by Shanin-Atidi and Bar-Eli.[21] The data listed in Table 1 show that the results obtained from the ^{1}H NMR agree very well with those received from the ^{13}C and ^{19}F NMR spectra. Thus the coalescence temperature approach seems to give reliable parameters for correlations of the structure with energy barrier heights. The usefulness of this method has been already demonstrated for various types of nitrosamines.[3c,d,22]

Due to a significant deviation of the nitrosamino chromophore from planarity the measured barriers to the N−N rotation are unusually low; in the case of the 1,5-dimethyl derivatives **3b**−**7b** they are almost two times lower than those reported for *N*-nitrosopiperidine and related nitrosamines.[3a−c] The activation energies $\Delta G^{\ddagger}$ for **1b** and **9b** are slightly higher than that determined for **3b** (by ca. 1 and 3 kcal/mol, respectively). The above trend parallels that observed in the UV spectra and points to the increasing pyramidal character of the N-3 nitrogen on going from **9b** to **1b** and **3b**. The compound **8b** substituted with 2,6-difluorophenyl groups shows the $\Delta G^{\ddagger}$ value ca. 1 kcal/mol higher than the related nitrosamine **3b**. Since the UV spectra suggest a comparable degree of pyramidalization of the amino nitrogen in both compounds, the enhancement of the energy barrier to the N−N rotation in **8b** can be attributed to a steric interference of the fluorine atoms with the nitroso oxygen.

At temperatures lower than required to "freeze" the N−N rotation, selective broadening and splitting of the signals corresponding to aryl groups occur in response

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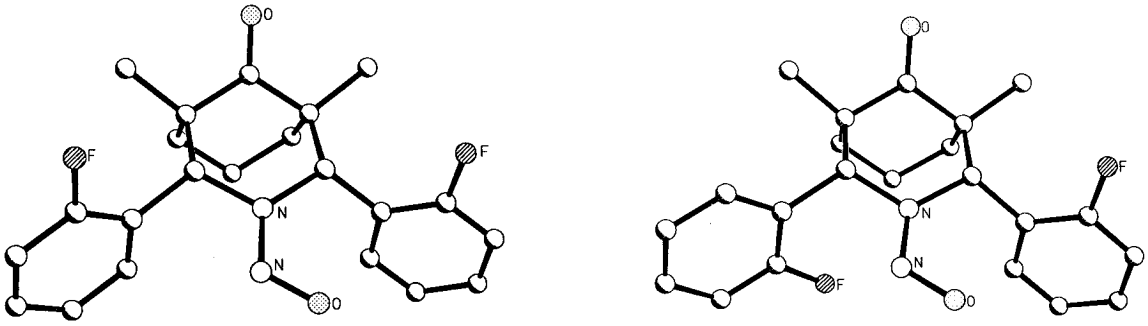

Figure 2. MM2 optimized geometries of two lowest energy conformers of **7b**.

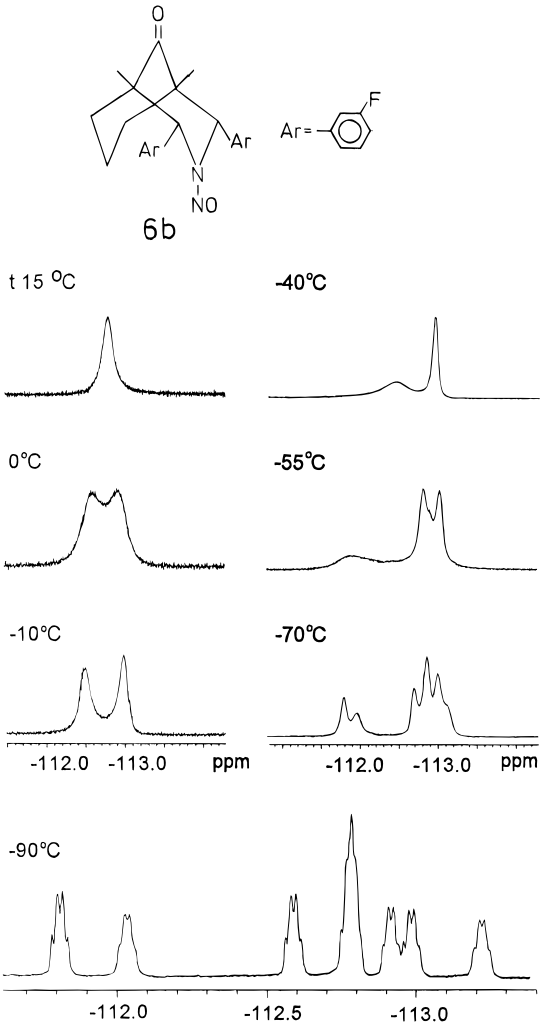

Figure 3. The variable temperature ^{19}F NMR spectra of **6b** in $(CD_3)_2CO$.

to slowing rotation of these substituents about the C−C bonds. The energy barriers for this process can be extracted from the DNMR spectra (Table 2). A steric interaction of the NO group with the rotating aryl rings should result in slightly different $\Delta G^{\ddagger}$ values for the substituents placed *syn* and *anti* to the nitroso oxygen. The inspection of the variable temperature ^{13}C NMR of **1b** (Figure 5 reveals splitting of the carbon line at 124.2 ppm below −40 °C. Since this signal is located upfield from the the remaining phenyl carbons the $\Delta G^{\ddagger}$ value of 10.9 kcal/mol, calculated from the spectra, was assigned to the *syn*-phenyl group. The estimation of the activation energy for the *anti*-phenyl substituent from the ^{13}C NMR spectrum is rather problematic because of its complexity. There is no such a difficulty in the case of compounds

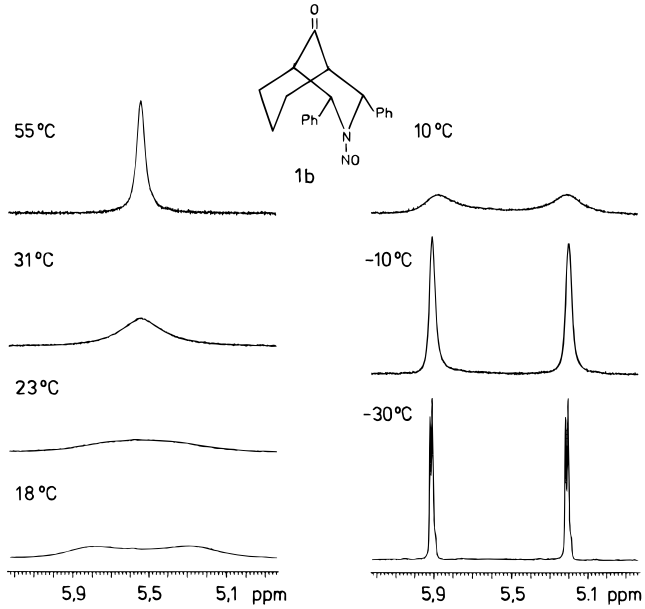

Figure 4. The variable temperature ^{1}H NMR spectra of **1b** (benzylic protons) in $CDCl_3$.

with appropriately substituted phenyl moieties, which give well separated signals of substituents corresponding to all possible rotamers involved in the conformational equilibrium. Especially useful appeared to be derivatives with meta-substituted phenyls, since the substituents at meta positions do not interfere with the nitroso oxygen and therefore should not affect substantially the rotation barriers. Thus observing the signals of the 3-methoxy methyl in the ^{1}H DNMR spectra of **4b** and the fluorine resonances in the ^{19}F DNMR of **6b** (Figure 3), we were able to assign the $\Delta G^{\ddagger}$ values for both aryl groups in these compounds. In the case of **6b**, two energy barriers of 10.8 and 9.8 kcal/mol corresponding to the *syn* and *anti*-3-fluorophenyls, respectively, were found in the $(CD_3)_2CO$ solution. It is noteworthy that the activation energy, determined in a similar way, for the 3-fluorophenyl group in the parent amine **6a** is considerably lower (9.1 kcal/mol). This finding demonstrates that the NNO group slows down the rotation of both *syn* and *anti*-aryl substituents and proves that the steric hindrance is caused not only by the nitroso oxygen but also by the nitrogen lone pair as well. The importance of the steric effect of the nitrogen lone pair on the conformation of nitrosamines has been reported on several occasions.[4e,23]

The rotation barrier of the 2,6-difluorophenyl groups was assigned from the decoalescence of two fluorine

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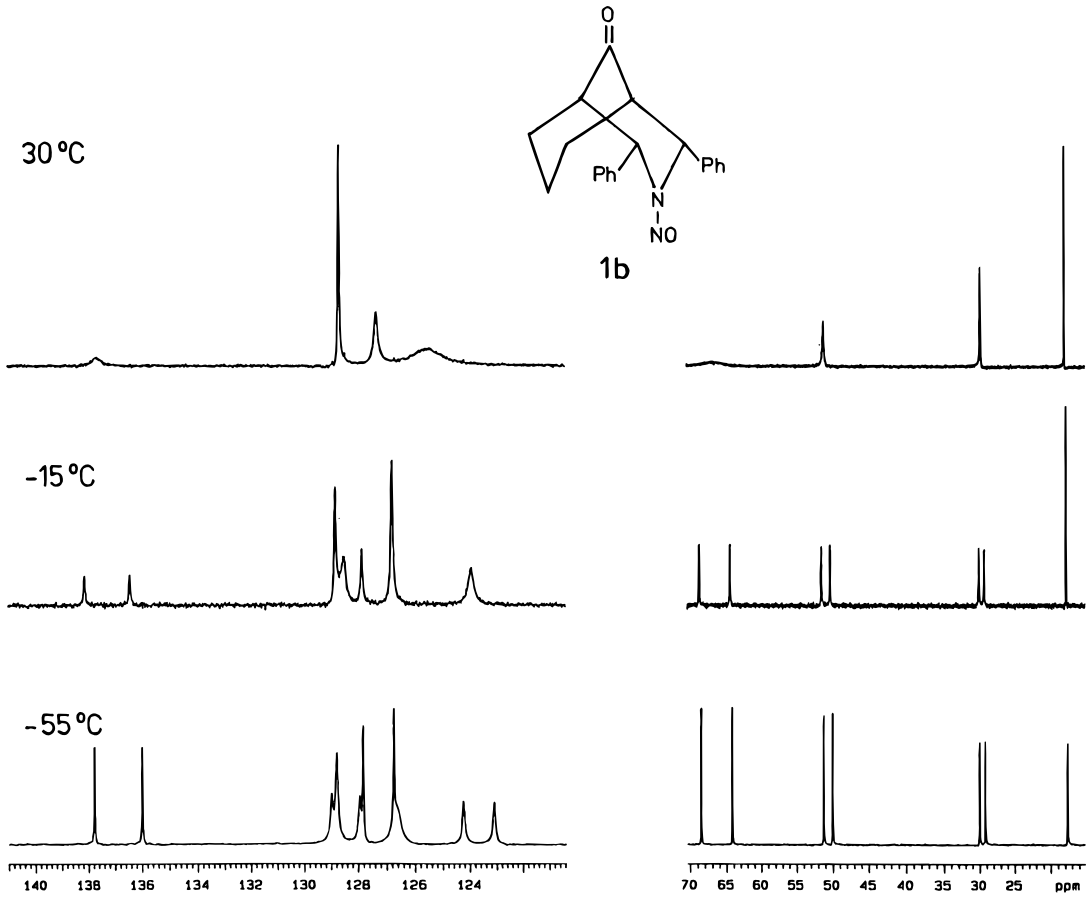

Figure 5. The variable temperature ^{13}C NMR spectra of **1b** in $CDCl_3$.

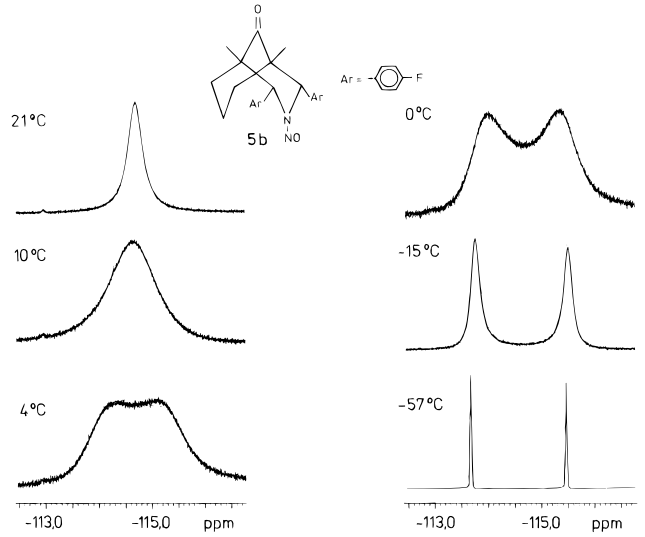

Figure 6. The variable temperature ^{19}F NMR spectra of **5b** in $CDCl_3$.

signals in **8a** at 116 °C, whereas raising of the temperature up to 160 °C did not result in the coalescence of the ^{19}F peaks in the nitrosamine **8b**. A further increase of temperature led to a decomposition of **8b**. The corresponding $\Delta G^{\ddagger}$ values are significantly higher than for the other aryl groups in the compounds studied; in the case of **8b** the estimated barrier height is >20.5 kcal/mol and therefore the C−C rotation of the 2,6-difluorophenyl rings appeared to be much slower than the N−N rotation of the NO group. On the basis of the MM2 calculations we attributed it to the steric interaction of the fluorine atoms with the methyl substituents at C-1 and C-5 and with the nitroso oxygen atom.

Table 1. Free Energies of Activation ($\Delta G^{\ddagger}$) for the N−N Rotational Process[a]

compd	solvent	resonance of nuclei	T_c (°C)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ kcal/mol)
1b	$CDCl_3$	^1H	21	282	13.4
		^{13}C	28	543	13.4
2b	$CDCl_3$	^1H	7	278	13.1[b]
		^{13}C	15	514	13.2[c]
3b	$CDCl_3$	^1H	0	178	12.7
		^{13}C	5	312	12.6
4b	$CDCl_3$	^1H	0	235	12.5
	$(CD_3)_2CO$	^1H	5	233	12.8
5b	$CDCl_3$	^1H	−6	190	12.4
		^{19}F	4	376	12.5
6b	$CDCl_3$	^1H	−4	141	12.6
		^{19}F	−5	120	12.7
	$(CD_3)_2CO$	^{19}F	3	145	12.9
7b	$CDCl_3$	^1H	−8	266	12.2
		^{19}F	7	643	12.3
8b	$CDCl_3$	^1H	22	144	13.9
		^{13}C	27	255	13.8
		^{19}F	2	32	13.7
9b	$CDCl_3$	^1H	34[d]	26	15.5
		^{13}C	40	587	15.3
10b	$CDCl_3$	^1H	42	293	14.8[e]
		^{13}C	50	632	14.6[f]

[a] The errors on $\Delta G^{\ddagger}$ are ±0.2 kcal/mol. [b] The average barrier $\Delta G^{\ddagger}_{ZE}$ = 12.8 kcal/mol, $\Delta G^{\ddagger}_{EZ}$ = 13.4 kcal/mol. [c] $\Delta G^{\ddagger}_{ZE}$ = 12.8 and $\Delta G^{\ddagger}_{EZ}$ = 13.5 kcal/mol. [d] For the protons at the C-1 and C-5. [e] $\Delta G^{\ddagger}_{ZE}$ = 14.5 and $\Delta G^{\ddagger}_{EZ}$ = 15.0 kcal/mol. [f] $\Delta G^{\ddagger}_{ZE}$ = 14.3 and $\Delta G^{\ddagger}_{EZ}$ = 14.9 kcal/mol.

In conclusion, the title compounds are rare examples of stable nonplanar *N*-nitrosamino systems. To relieve the $A^{(1,3)}$ strain imposed by the steric interaction of the NNO group with the neighboring equatorial aryl sub-

Table 2. Free Energies of Activation ($\Delta G^{\ddagger}$) for the C−C Rotation of the Aryl Group[a]

compd	solvent	resonance of nuclei	T_c (°C)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (kcal/mol)
1b	$CDCl_3$	^{13}C	−40	134	10.8
4a	$(CD_3)_2CO$	^{1}H	−89	19	9.2
4b	$(CD_3)_2CO$	^{1}H	−71	15	10.3
			−88	14	9.4
6a	$(CD_3)_2CO$	^{19}F	−68	453	9.1[b]
6b	$(CD_3)_2CO$	^{19}F	−50	53	10.8
			−50	470	9.8
8a	$C_6D_5NO_2$	^{19}F	116	158	18.4
8b	$C_6D_5NO_2$	^{19}F	>160[c]	2260	>18.3
		^{1}H	>160[c]	188	>20.5

[a] The errors on $\Delta G^{\ddagger}$ are ±0.3 kcal/mol. [b] The average barrier. [c] A decomposition of **8b** occurs above 160 °C.

stituents the molecules enhance a pyramidal character of the amino nitrogen observed in the X-ray crystallographic structures. A significant deviation of the nitrosamino chromophore from planarity results in a bathochromic shift of the n−π* absorption maxima in the UV spectra and a considerable lowering of the N−N rotation barriers shown by the DNMR spectra.

Experimental Section

^{1}H, ^{13}C, and ^{19}F NMR spectra were measured at 500, 126, and 470 MHz, respectively, using a temperature control accessory. The deuteriated solvents were used as an internal lock for ^{1}H and ^{13}C NMR. The ^{19}F chemical shifts were referenced to the external $CFCl_3$ standard. The amines **1a**−**10a** were obtained according to the modified literature procedures.[13]

2,4-Diphenyl-3-azabicyclo[3.3.1]nonan-9-one (1a). Ammonium acetate (7.7 g, 100 mmol) was dissolved in boiling methanol (50 mL) and added to the mixture of cyclohexanone (12.0 mL, 120 mmol) and benzaldehyde (21.1 mL, 200 mmol). The reaction mixture was left to stand overnight at room temperature. The precipitated crystals were filtered, washed with methanol, and recrystallized from toluene−heptane: yield 8.5 g (29%); mp 185−187 °C (lit.[13b] mp 184−185 °C); ^{1}H NMR ($CDCl_3$) δ 7.59 (m, 4 H), 7.44 (m, 4 H), 7.35 (m, 2H), 4.43 (d, J = 2.7 Hz, 2 H), 2.94 (m, 1 H), 2.51 (m, 2 H), 1.96 (m, 2 H), 1.74 (m, 2 H), 1.62 (br s, 1 H), 1.42 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 217.4, 141.2, 128.5, 127.5, 126.8, 64.7, 53.9, 29.0, 21.1.

1-Methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one (2a) was obtained in a manner similar to that of compound **1a**: mp 120−122 °C (from toluene−heptane) (lit.[13b] mp 120−121 °C); ^{1}H NMR ($CDCl_3$) δ 7.62−7.28 (complex m, 10 H), 4.44 (d, J = 3.0 Hz, 1 H), 3.99 (s, 1 H), 3.23 (m, 1 H), 2.62 (m, 1 H), 2.13 (m, 1 H), 1.97 (m, 1 H), 1.88 (br s, 1 H), 1.74 (m, 1 H), 1.50 (m, 2 H), 0.86 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 217.7, 141.1, 139.7, 129.0, 128.3, 127.9, 127.8, 127.3, 126.7, 71.1, 64.8, 54.3, 50.7, 36.7, 29.0, 21.3, 20.2.

1,5-Dimethyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one (3a). A solution of ammonium acetate (1.9 g, 25 mmol), benzaldehyde (5.3 mL, 50 mmol), and 2,6-dimethylcyclohexanone (4.4 mL, 35 mmol) (Aldrich, mixture of isomers) was refluxed in methanol for 8 h. After the reaction mixture was cooled, the precipitated crystals were filtered, washed with methanol, and recrystallized from toluene: yield 3.7 g (42%); mp 197−199 °C; ^{1}H NMR ($CDCl_3$) δ 7.55 (m, 4 H), 7.40−7.30 (m, 6 H), 3.94 (s, 2 H), 3.48 (m, 1 H), 2.12 (m, 2 H), 1.86 (br s, 1 H), 1.50 (m, 3 H), 0.85 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 217.8, 139.7, 128.8, 127.8, 127.6, 50.8, 36.8, 21.3, 20.7. Anal. Calcd for $C_{22}H_{25}NO$ (319): C, 82.72; H, 7.89; N, 4.38. Found: C, 82.69; H, 7.94; N, 4.44.

1,5-Dimethyl-2,4-bis(3-methoxyphenyl)-3-azabicyclo[3.3.1]nonan-9-one (4a) was obtained in a manner similar to that of compound **3a**: mp 188−189 °C (from toluene−heptane); ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 2 H), 7.11 (m, 4 H), 6.86 (m, 2 H), 3.89 (s, 2 H), 3.84 (s, 6 H), 3.45 (m, 1 H), 2.16 (m, 2 H), 1.86 (br s, 1 H), 1.49 (m, 3 H), 0.85 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 217.7, 159.2, 141.3, 128.8, 121.5, 115.1, 112.4, 71.3, 55.1, 50.8, 36.9, 21.3, 20.8. Anal. Calcd for $C_{24}H_{29}NO_3$ (379): C, 75.96; H, 7.70; N, 3.69. Found: C, 76.00; H, 8.06; N, 3.79.

1,5-Dimethyl-2,4-bis(4-fluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one (5a) was obtained in a manner similar to that of compound **3a**: mp 187−188 °C (from toluene−heptane); ^{1}H NMR ($CDCl_3$) δ 7.50 (dd, 4 H, J = 3.3 and 5.6 Hz), 7.06 (t, J = 8.7 Hz, 4 H), 3.92 (s, 2 H), 3.38 (m, 1 H), 2.07 (m, 2 H), 1.82 (br s, 1 H), 1.50 (m, 3 H), 0.82 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 217.3, 162.3 (d, J_{CF} = 246.3 Hz), 135.3, 130.3 (d, J_{CF} = 7.7 Hz), 114.8 (d, J_{CF} = 21.4 Hz), 70.7, 50.8, 36.6, 21.3, 20.7; ^{19}F NMR ($CDCl_3$) δ −114.9. Anal. Calcd for $C_{22}H_{23}NOF_2$ (355): C, 74.34; H, 6.52; N, 3.94. Found: C, 74.14; H, 6.57; N, 3.87.

1,5-Dimethyl-2,4-bis(3-fluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one (6a) was obtained in a manner similar to that of compound **3a**: mp 230−231 °C (from toluene); ^{1}H NMR ($CDCl_3$) δ 7.38−7.26 (m, 6 H), 7.05 (td, J = 2.4 and 8.3 Hz, 2 H), 3.96 (s, 2 H), 3.40 (m, 1 H), 2.11 (m, 2 H), 1.91 (br s, 1 H), 1.54 (m, 3 H), 0.88 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 217.0, 162.6 (d, J_{CF} = 245.5 Hz), 142.1 (d, J_{CF} = 6.8 Hz), 129.4 (d, J_{CF} = 8.4 Hz), 124.7, 115.7 (d, J_{CF} = 21.4 Hz), 114.8 (d, J_{CF} = 21.0 Hz), 70.9, 50.8, 36.8, 21.4, 20.8; ^{19}F NMR ($CDCl_3$) δ −113.5. Anal. Calcd for $C_{22}H_{23}NOF_2$ (355): C, 74.34; H, 6.52; N, 3.94. Found: C, 74.41; H, 6.80; N, 4.01.

1,5-Dimethyl-2,4-bis(2-fluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one (7a) was obtained in a manner similar to that of compound **3a**: mp 154−156 °C (from toluene−heptane); ^{1}H NMR ($CDCl_3$) δ 7.92 (td, J = 2,1 and 7.2 Hz, 2 H), 7.25 (m, 4 H), 7.05 (m, 2 H), 4.45 (s, 2 H), 3.42 (m, 1 H), 2.18 (m, 2 H), 1.52 (m, 4 H), 0.88 (d, J_{HF} = 3.0 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 216.9, 160.4 (d, J_{CF} = 247.5 Hz), 129.9 (d, J_{CF} = 3 Hz), 129.0 (d, J_{CF} = 8.7 Hz), 127.0 (d, J_{CF} = 12.1 Hz), 123.9, 115.2 (d, J_{CF} = 22.8 Hz), 62.0, 51.1, 37.2, 21.5, 19.9; ^{19}F NMR ($CDCl_3$) δ −115.5. Anal. Calcd for $C_{22}H_{23}NOF_2$ (355): C, 74.34; H, 6.52; N, 3.94. Found: C, 74.12; H, 6.53; N, 3.80.

1,5-Dimethyl-2,4-bis(2,6-difluorophenyl)-3-azabicyclo-[3.3.1]nonan-9-one (8a) was obtained in a manner similar to that of compound **3a**: mp 196 °C (from EtOH); ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 2 H), 6.95 (m, 4 H), 4.46 (d, J = 13.7 Hz, 2 H), 4.33 (m, 1 H), 2.95 (m, 1 H), 2.29 (m, 2 H), 1.72 (m, 3 H), 0.95 (d, J_{HF} = 2.9 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 216.3, 161.9 (dd, J_{CF} = 5.6 and 245.6 Hz), 160.6 (dd, J_{CF} = 11.0 and 248.5 Hz), 129.5 (t, J_{CF} = 11.2 Hz), 114.1 (t, J_{CF} = 18.0 Hz), 111.8 (t, J_{CF} = 25.0 Hz), 62.6 (d, J_{CF} = 2.7 Hz), 52.5, 37.5, 20.6 (t, J_{CF} = 5.9 Hz), 20.1; ^{19}F NMR ($CDCl_3$) δ −109.7, −111.7. Anal. Calcd for $C_{22}H_{21}NOF_4$ (391): C, 67.51; H, 5.41; N, 3.58. Found: C, 67.42; H, 5.50; N, 3.56.

2,4-Diphenyl-3-azabicyclo[3.3.1]nonane (9a) was obtained by Wolff−Kishner reduction of ketone **1a** according to the literature procedure:[13] mp 128−129 °C (from MeOH) (lit.[13a] mp 128−129 °C); ^{1}H NMR ($CDCl_3$) δ 7.55 (m, 4 H), 7.37 (m, 4 H), 7.25 (m, 2 H), 4.35 (d, J = 2.5 Hz, 2 H), 2.67 (m, 1 H), 2.15−1.95 (m, 2 H), 1.86 (m, 2 H), 1.62 (br s, 1 H), 1.55−1.30 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 145.4, 128.0, 126.8, 126.5, 65.3, 37.1, 35.1, 26.1, 22.1.

1-Methyl-2,4-diphenyl-3-azabicyclo[3.3.1]nonane (10a) was obtained from ketone **2a** in a manner similar to that of compound **9a**: mp 99−101 °C (from MeOH); ^{1}H NMR ($CDCl_3$) δ 7.55 (m, 4 H), 7.38 (m, 4 H), 7.30 (m, 2 H), 4.34 (d, J = 2.0 Hz, 1 H), 3.91 (s, 1 H), 2.93 (m, 1 H), 2.00 (m, 1 H), 1.89 (m, 1 H), 1.75 (m, 1 H), 1.72 (m, 1 H), 1.62 (br s, 1 H), 1.56 (m, 1 H), 1.46 (m, 1 H), 1.31 (m, 1 H), 1.08 (m, 1 H), 0.73 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 145.1, 143.0, 129.0, 128.0, 127.6, 127.0, 126.7, 126.5, 72.1, 65.4, 45.2, 36.8, 33.5, 32.7, 29.0, 25.6, 22.2. Anal. Calcd for $C_{21}H_{25}N$ (291): C, 86.55; H, 8.65; N, 4.81. Found: C, 86.29; H, 8.89; N, 4.55.

3-Azabicyclo[3.3.1]nonane (11a) was obtained by $LiAlH_4$ reduction of *cis*-cyclohexane-1,3-dicarboximide; after sublimation mp 158−159 °C (lit.[24] 144−146 °C); ^{1}H NMR ($CDCl_3$) δ 3.07 (s, 4 H), 2.22 (m, 1 H), 1.99 (br s, 1 H), 1.85−1.62 (complex m, 9 H); ^{13}C NMR ($CDCl_3$) δ 52.1, 33.9, 31.0, 28.6, 23.1; hydrochloride mp 278−280 °C; ^{1}H NMR ($CDCl_3$) δ 9.81 (br s, 1 H), 8.48 (br s, 1 H), 3.36 (d, J = 13.1 Hz, 2 H), 3.18 (dd, J =

(24) Komppa, G. *Chem. Ber.* **1932**, *65*, 792.

3.2 and 13.1 Hz, 2 H), 2.26 (m, 1 H), 2.04 (m, 2 H), 1.91 (m, 2 H), 1.70 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 46.9, 30.1, 28.9, 25.4, 19.8.

***N*-Nitroso-2,4-diphenyl-3-azabicyclo[3.3.1]nonan-9-one (1b).** To a solution of amine **1a** (1.45 g, 5 mmol) in chloroform (10 mL) were added concd hydrochloric acid (1.5 mL) and water (1.5 mL), and while stirring, solid $NaNO_2$ (0.84 g, 12 mmol) was added in portions during 0.5 h. The stirring was continued for another 0.5 h. The organic layer was washed with water and saturated $NaHCO_3$ and dried over $MgSO_4$. After evaporation of the chloroform, the residue was crystallized from toluene−heptane: yield 1.22 g (76%); mp 168−169 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.45−7.25 (m, 10 H), 5.55 (br s, 2 H), 2.90 (m, 2 H), 2.03 (m, 1 H), 1.68 (m, 4 H), 1.38 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 212.9, 137.7 (br), 128.8, 127.4, 125.6 (br), 66.9 (br), 51.3, 29.9, 18.2; UV (cyclohexane) λ_{max} 410 nm (ϵ 87). Anal. Calcd for $C_{20}H_{20}N_2O_2$ (320): C, 74.98; H, 6.29; N, 8.74. Found: C, 74.65; H, 6.39; N, 8.63.

***N*-Nitroso-1-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]-nonan-9-one (2b)** was obtained from amine **2a** in a manner similar to that of compound **1b**: mp 162−163 °C (from MeOH); ^{1}H NMR ($CDCl_3$) δ 7.55−7.15 (complex m, 10 H), 5.32 (br s, 1 H), 5.08 (br s, 1 H), 2.98 (m, 1 H), 2.30 (m, 1 H), 1.94 (m, 1 H), 1.67 (m, 2 H), 1.48 (m, 2 H), 1.11 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 213.8, 137.2, 136.7, 128.7, 128.4, 128.0, 127.2, 125.1 (br), 74.5 (br), 65.8 (br), 50.9, 49.5, 37.3, 30.3, 21.5, 19.2; UV (cyclohexane) λ_{max} 413 nm (ϵ 78). Anal. Calcd for $C_{21}H_{22}N_2O_2$ (334): C, 75.42; H, 6.63; N, 8.38. Found: C, 75.17; H, 6.66; N, 8.43.

***N*-Nitroso-1,5-dimethyl-2,4-diphenyl-3-azabicyclo[3.3.1]-nonan-9-one (3b)** was obtained from amine **3a** in a manner similar to that of compound **1b**: mp 174−175 °C dec (from toluene); ^{1}H NMR ($CDCl_3$) δ 7.42 (m, 10 H), 4.89 (br s, 2 H), 2.65 (m, 1 H), 1.88 (m, 2 H), 1.54 (m, 3 H), 1.15 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 214.3, 136.4, 128.2, 127.5, 73.5 (br), 48.9, 37.5, 21.9, 19.9; UV (cyclohexane) λ_{max} 417 nm (ϵ 85). Anal. Calcd for $C_{22}H_{22}N_2O_2$ (348): C, 75.83; H, 6.94; N, 8.04. Found: C, 75.86; H, 6.99; N, 8.11.

***N*-Nitroso-1,5-dimethyl-2,4-bis(3-methoxyphenyl)-3-azabicyclo[3.3.1]nonan-9-one (4b)** was obtained from amine **4a** in a manner similar to that of compound **1b**: mp 167 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.36 (t, J = 7.8 Hz, 2 H), 7.08 (m, 2 H), 7.01 (m, 2 H), 6.91 (dd, J = 2.0 and 7.8 Hz, 2 H), 4.88 (br s, 2 H), 3.87 (s, 6 H), 2.63 (m, 1 H), 1.96 (m, 2 H), 1.62 (m, 1 H), 1.51 (m, 2 H), 1.19 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 214.3, 159.4, 138.0, 129.2, 120.0, 114.2, 112.3, 73.4 (br), 55.1, 48.9, 37.6, 22.1, 19.9; UV (cyclohexane−dioxane, 4:1) λ_{max} 412 nm (ϵ 78). Anal. Calcd for $C_{24}H_{28}N_2O_4$ (408): C, 70.57; H, 6.91; N, 6.86. Found: C, 70.55; H, 6.97; N, 6.90.

***N*-Nitroso-1,5-dimethyl-2,4-bis(4-fluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one (5b)** was obtained from amine **5a** in a manner similar to that of compound **1b**: mp 189 °C dec (from toluene); ^{1}H NMR ($CDCl_3$) δ 7.39 (m, 4 H), 7.12 (t, J = 8.6 Hz, 4 H), 4.82 (br s, 2 H), 2.54 (m, 1 H), 1.86 (m, 2 H), 1.62 (m, 1 H), 1.52 (m, 2 H), 1.11 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 213.9, 162.1 (d, J_{CF} = 246.1 Hz), 132.1, 129.1 (d, J_{CF} = 7.8 Hz), 115.3 (d, J_{CF} = 22.2 Hz), 72.9 (br), 49.0, 37.4, 21.8, 20.1; ^{19}F NMR ($CDCl_3$) δ −114.7; UV (cyclohexane−dioxane, 4:1) λ_{max} 414 nm (ϵ 90). Anal. Calcd for $C_{22}H_{22}N_2O_2F_2$ (384): C, 68.74; H, 5.77; N, 7.29. Found: C, 68.85; H, 5.70; N, 7.13.

***N*-Nitroso-1,5-dimethyl-2,4-bis(3-fluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one (6b)** was obtained from amine **6a** in a manner similar to that of compound **1b**: mp 180 °C dec (from toluene); ^{1}H NMR ($CDCl_3$) δ 7.43 (m, 2 H), 7.24 (m, 2 H), 7.16 (m, 2 H), 7.09 (t, J = 8.3 Hz, 2 H), 4.84 (br s, 2 H), 2.57 (m, 1 H), 1.93 (m, 2 H), 1.70 (m, 1 H), 1.67 (m, 2 H), 1.17 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 213.6, 162.7 (d, J_{CF} = 246.0 Hz), 138.8 (d, J_{CF} = 3.0 Hz), 129.9 (d, J_{CF} = 7.9 Hz), 123.4, 114.8 (d, J_{CF} = 21.2 Hz), 73.0 (br), 48.9, 37.5, 21.9, 20.1; ^{19}F NMR ($CDCl_3$) δ −112.8 (br); UV (cyclohexane−dioxane, 4:1) λ_{max} 414 (ϵ 88). Anal. Calcd for $C_{22}H_{22}N_2O_2F_2$ (384): C, 68.74; H, 5.77; N, 7.29. Found; C, 69.02; H, 5.82; N, 7.21.

***N*-Nitroso-1,5-dimethyl-2,4-bis(2-fluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one (7b)** was obtained from amine **7a** in a manner similar to that of compound **1b**: mp 182 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.62 (br, 2 H), 7.36 (m, 2 H), 7.20 (m, 4 H), 5.17 (br s, 2 H), 2.77 (m, 1 H), 2.11 (m, 2 H), 1.75 (m, 1 H), 1.61 (m, 2 H), 1.10 (d, J_{HF} = 3.4 Hz, 6 H); ^{13}C NMR ($CDCl_3$) δ 212.6, 159.9 (d, J_{CF} = 246.4 Hz), 129.2, 127.9 (br), 123.8 (d, J_{CF} = 3.0 Hz), 116.0 (d, J_{CF} = 23.1 Hz), 64.6 (br), 49.6, 37.9, 21.0, 20.2; ^{19}F NMR ($CDCl_3$) δ −114.6 (br s, 1 F), −108.4 (br s, 1 F); UV (cyclohexane−dioxane, 4:1) λ_{max} 416 nm (ϵ 88). Anal. Calcd for $C_{22}H_{22}N_2O_2F_2$ (384): C, 68.74; H, 5.77; N, 7.29. Found: C, 68.60; H, 5.85; N, 7.22.

***N*-Nitroso-1,5-dimethyl-2,4-bis(2,6-difluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one (8b)** was obtained from amine **8a** in a manner similar to that of compound **1b**: mp 181 °C dec (from toluene); ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 2 H), 6.97 (m, 4 H), 5.05 br s, 2 H), 2.17 (m, 2 H), 1.60 (m, 3 H), 1.03 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 213.4, 129.5 (br), 112.1 (br), 111.5 (dd, J_{CF} = 3.3 and 24.5 Hz), 63.2 (br), 50.8, 38.6, 20.4, 18.5 (t, J_{CF} = 13.0 Hz); ^{19}F NMR ($CDCl_3$, 5 °C) δ −103.6 (s, 1 F), −110.3 (s, 2 F), −111.4 (s, 1 F); UV (cyclohexane−dioxane, 4:1) λ_{max} 412 (ϵ 94). Anal. Calcd for $C_{22}H_{20}N_2O_2F_4$ (421): C, 62.79; H, 4.79; N, 6.66. Found: C, 62.84; H, 4.70; N, 6.70.

***N*-Nitroso-2,4-diphenyl-3-azabicyclo[3.3.1]nonane (9b)** was obtained from amine **9a** in a similar manner to that of compound **1b**: mp 166−167 °C (from MeOH); ^{1}H NMR ($CDCl_3$) δ7.60−7.10 (complex m, 10 H), 5.71 (br s, 1 H), 4.95 (br s, 1 H), 2.52 (m, 1 H), 2.43 (m, 1 H), 2.05 (m, 2 H), 1.62 (m 1 H), 1.53 (m, 1 H), 1.37 (m, 1 H), 1.27 (m, 2 H), 1.12 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 141.4, 139.8, 128.5, 128.3, 127.0, 126.8, 126.1, 124.1, 68.7, 64.1, 34.6, 33.9, 32.1, 31.6, 31.1, 27.1, 26.3, 18.8; UV (cyclohexane) λ_{max} 405 nm (ϵ 88). Anal. Calcd for $C_{20}H_{22}N_2O$ (306): C, 78.40; H, 7.24; N, 9.14. Found: C, 78.31; H, 7.28; N, 9.24.

***N*-Nitroso-1-methyl-2,4-diphenyl-3-azabicyclo[3.3.1]-nonane (10b)** was obtained from amine **10a** in a similar manner to that of compound **1b**: mp 139 °C (from MeOH); ^{1}H NMR ($CDCl_3$) δ 7.60−7.05 (complex m, 10 H), 5.67 (br s, 0.7 H), 5.07 (br s, 0.7 H), 4.88 (br s, 0.7 H), 4.49 (br s, 0.3 H), 2.58 (m, 1 H), 1.84 (m, 3 H), 1.70−1.10 (comlex m, 5 H), 1.07 (s, 0.9 H), 1.06 (s, 2.1 H); ^{13}C NMR ($CDCl_3$) δ 139.2 (br), 129.0, 128.1, 127.4, 126.6 (br), 125.9, 124.1, 75.7, 70.7 (br), 68.1 (br), 63.5, 39.7, 34.4, 34.0, 33.3, 30.2, 26.7, 25.9, 19.6; UV (cyclohexane) λ_{max} 413 nm (ϵ 78). Anal. Calcd for $C_{21}H_{24}N_2O$ (320): C, 78.72; H, 7.55, N, 8.74. Found: C, 78.75; H, 7.72; N, 8.77.

***N*-Nitroso-3-azabicyclo[3.3.1]nonane (11b)** was obtained from amine **11a** by N-nitrosation with HNO_2: mp 164−166 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 4.92 (m, 1 H), 4.78 (m, 1 H), 3.95 (m, 1 H), 3.93 (m, 1 H), 2.74 (m, 1 H), 2.18 (m, 1 H), 2.08 (m, 1 H), 1.92 (m, 1 H), 1.86 (m, 2 H), 1.80−1.55 (complex m, 3 H), 1.40 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 55.6, 44.7, 32.3, 30.9, 30.0, 28.1, 27.2, 18.5; UV (cyclohexane) λ_{max} 365 nm (ϵ 135). Anal. Calcd for $C_8H_{14}N_2O$ (154): C, 62.31; H, 9.15; N, 18.17. Found: C, 62.03; H, 9.41; N, 17.91.

X-ray Diffraction Analysis. Crystal data for $C_{22}H_{24}N_2O_2$ (**3b**): orthorhombic, space group *Pnma*, a = 8.043(2) Å, b = 20.900(4) Å, c = 11.094(2) Å, V = 1864.9(7) Å^3, Z = 4, D_{calcd} = 1.241 g cm^{-3}, λ(Cu Kα_1) = 1.54178 Å, T = 293 K, R = 0.036 for 1643 independent reflections with $I > 2\sigma(I)$. Crystal data for $C_{22}H_{20}F_4N_2O_2$ (**8b**): orthorhombic, $P2_12_12_1$, a = 7.873(2) Å, b = 11.391(2) Å, c = 21.706(4) Å, V = 1946.6(7) Å^3, Z = 4, D_{calcd} = 1.434 g cm^{-3}, λ(Cu Kα_1) = 1.54178 Å, T = 293 K, R = 0.032 for 3322 independent reflections with $I > 2\sigma(I)$.

Acknowledgment. We we wish to thank to Dr. P. Sowiński for many helpful discussions, Mrs. J. Woszczyk and Mr. W. Ciesielski (PAN Łódź) for variable temperature NMR measurements.

Supporting Information Available: The ORTEP drawing of the X-ray structure of **3b**, the variable temperature ^{1}H and ^{19}F NMR spectra of **4b** and **7b**, respectively, and UV-vis spectra of **3b** and **11b** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from ACS. Ordering information is given on any current masthead page.

JO9600159