Conformation and Stereodynamics of *N,N′*-Dinitroso-2,4,6,8-tetraaryl-3,7-diazabicyclo[3.3.1]nonanes[1]

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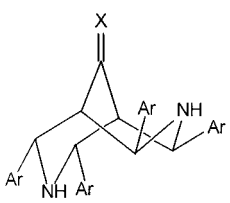
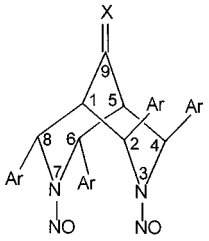
The conformational studies of *N*-nitrosamines have received a great deal of attention in recent years because of their biological importance.[2] The NO group introduced at the nitrogen atom of a heterocyclic system can dramatically influence the ring conformation and the orientation of substituents. The conformational changes result from the allylic $A^{(1,3)}$ strain,[3] caused by a steric interference of the NNO moiety with the neighboring α-substituents. Recently, we have shown that this kind of interaction is responsible for destabilization of the diequatorial chair conformation of *N*-nitroso-*cis*-2,6-diphenylpiperidines and the preference of diaxial orientation of phenyl substituents.[4]

In this paper we describe conformational effects caused by the *N*-nitrosation of 2,4,6,8-tetraaryl-3,7-diazabicyclo-[3.3.1]nonanes **1a**−**4a**. These bicyclic systems (bispidines) are among the most thoroughly investigated hetero analogues of bicyclo[3.3.1]nonane.[5] The compounds **1a**−**3a** are easily accessible from Mannich condensation of acetone with corresponding benzaldehyde and ammonium acetate, whereas the amine **4a** can be obtained by Wolff−Kishner reduction of **1a**.[6] Their bicyclic skeleton assumes an unusual chair−boat conformation, which is stabilized by four equatorially located aryl substituents, as evidenced by the X-ray diffraction data and various NMR experiments.[7] However, we expected that the *N*-nitrosation of two amino groups in **1a**−**4a** should lead to strong destabilization of this structure due to the $A^{(1,3)}$ strain brought about by a nearly coplanar location of the NNO moieties and the neighboring equatorial aryl groups. Thus we prepared *N*-nitrosamines **1b**−**4b** and studied their conformation by the molecular mechanics (MM2) calculations, NMR spectroscopy, and X-ray crystallography. With the aid of variable temperature ^1H and ^{19}F NMR measurements, we found two different barriers to the N−N rotation for each compound, resulted from different geometries at the N-3 and N-7 amino nitrogens.





1a Ar = Ph, X = O
2a Ar = Me-pC_6H_4, X = O
3a Ar = F-pC_6H_4, X = O
4a Ar = Ph, $X = H_2$

1b Ar = Ph, X = O
2b Ar = Me-pC_6H_4, X = O
3b Ar = F-pC_6H_4, X = O
4b Ar = Ph, $X = H_2$

Results and Discussion

The molecular mechanics (MM2) calculations[8] for the title dinitrosamines predicted two energy minima: one for a chair−boat conformer and the second one for a chair−chair conformer, with two phenyls occupying the equatorial positions and the remaining two in the axial locations. The latter is preferred by 6.7 and 4.7 kcal/mol in the cases of compounds **1b** and **4b**, respectively. A primary reason of this enormous energy difference between the conformers is the strong $A^{(1,3)}$ strain in the chair−boat form, which prevails over the axial−axial steric interaction of the phenyl rings in the twin-chair form. The second reason, pointed by McCabe and coworkers,[9] is the reduced 3,7 electron lone pair repulsion in 3,7-diazabicyclo[3.3.1]nonanes caused by substituents inducing sp^2 hybridization at the nitrogen atoms. Therefore introduction of two NO groups into amines **1a**−**4a** should change their skeleton conformations from the chair−boat to the twin-chair one and force the substituents in one ring to a diaxial orientation. It is noteworthy that the above geometry changes relieves the $A^{(1,3)}$ strain only in one ring of the nitrosamine molecule, whereas it remains in the second ring, since its inversion and reorientation of the substituents is impossible. However, by analogy with related *N*-nitroso-2,4-diaryl-3-azabicyclo[3.3.1]nonanes[10] it is expected that the $A^{(1,3)}$ strain in the second ring can be avoided by a distortion of the nitrosamine group from planarity, because a pyramidalization of the N-3 amino nitrogen diminishes spatial proximity between the NO group and the equatorial aryl substituents.

The X-ray crystallographic analysis of a single crystal of **1b**, obtained by a slow evaporation from ethanol, revealed two molecules (assigned as A and B) in the asymmetric unit.[11] Their geometric features are very similar: the bicyclic skeleton indeed adopts the twin-chair conformation (Figure 1), one nitrosamino group is significantly deviated from planarity [the N-3 atom is displaced by 0.335(3) and 0.307(4) Å in the molecule A and B, respectively, from the plane containing three

[†] A. Mickiewicz University.

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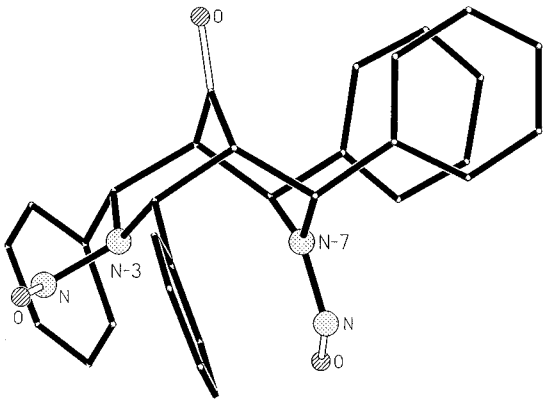

Figure 1. The molecular structure of **1b**.

neighboring atoms], whereas the second one is essentially planar (the N-7 atom is less than 0.05 Å out of the plane).

Different character of two nitrosamine chromophores contained in the title compounds are manifested by their UV-vis spectra. They exhibit two weak n−π* absorption bands: one structureless at 410 nm and the second one with a pronounced fine structure at 385 nm. The first one resembles that exhibited by the aforementioned *N*-nitroso-2,4-diaryl-3-azabicyclo[3.3.1]nonanes and corresponds to the electronic excitation in the nonplanar nitrosamine chromophore,[10a] whereas the second one, at shorter wavelengths, is similar to that shown by typical *N*-nitrosamines[12] and can be assigned to the planar nitrosamine moiety.

The ^{1}H NMR spectra afford additional evidence of the twin-chair geometry of the nitrosamine skeleton in solution. It is known, that due to a strong shielding anisotropy of the NNO group, the α-equatorial hydrogens in *N*-nitrosopiperidines are further downfield from the corresponding axial ones.[13] Thus in the spectrum of **1b** the benzylic proton signals observed at 6.19 and 6.61 ppm must be assigned to the ring with axial phenyl groups, and those at 5.52 and 5.57 ppm to the ring with equatorial substituents. Moreover, in the case of **4b**, a close proximity of the axial phenyl groups to one of the methylene hydrogens at C-9 results in its significant down shifting to 3.05 ppm. The NOE experiment shows that a selective irradiation of this proton produces a 12% enhancement of the signal at 6.57 ppm arising from the *ortho*-hydrogens in the axial phenyl rings.

The planar nitrosamine group is characterized by a relatively high energy barrier to the N−N rotation (roughly 23 kcal/mol)[14] owing to partial double bond

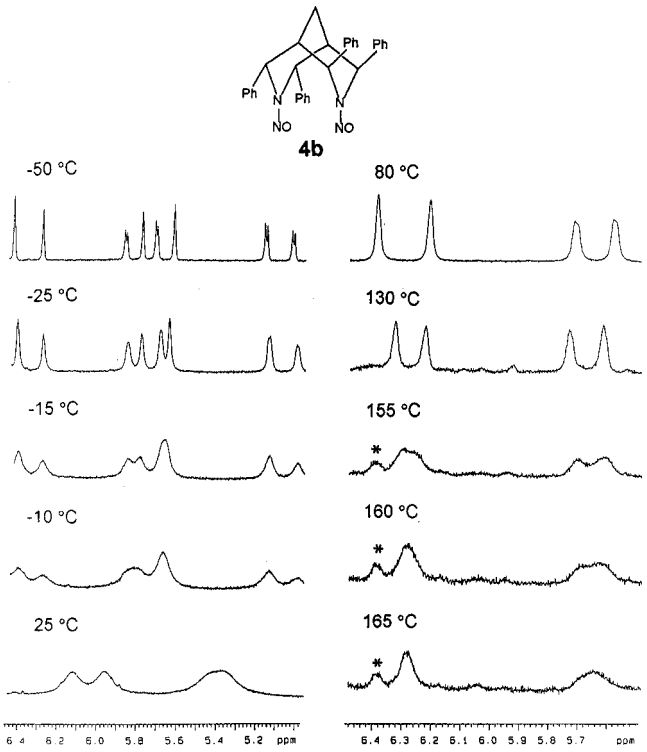

Figure 2. Temperature dependence of the benzylic ^{1}H signals (500 MHz) of **4b** in $CDCl_3$ (left) and $C_6D_5NO_2$ (right). The signal indicated by the asterisk is due to a decomposition product.

character between two adjacent nitrogen atoms. A deviation of this group from planarity decreases the n_N−π_{NO}* conjugation,[15] which results in weakenig of the N−N rotation barriers.[15,16] The observed nonequivalence of the benzylic protons at C-2 and C-4, and at C-6 and C-8, in compounds **1b**−**4b** is solely due to a slow, on the NMR time scale, N−N rotation in the planar nitrosamine moiety, whereas the second NO group bonded to the pyramidal N-3 amino nitrogen is expected to rotate relatively fast at room temperature and thus it cannot cause splitting of these signals. Similarly, the corresponding benzylic carbon atoms give rise to four distinct resonances in the ^{13}C NMR spectra. The benzylic proton signals in the nitrosamines **1b**−**4b** are slightly broadened due to slowing N−N rotation and lowering of the temperature results in their decoalescence (Figure 2). In effect eight benzylic resonances of different intensities, corresponding to unequally populated stereoisomers with *syn* and *anti* mutual orientations of two nitroso oxygens, appear in the spectrum below −40 °C. On the other hand, as the temperature is raised and the rate of internal rotation increases, initial sharpening of these signals is quickly followed by their broadening, because the N−N rotation in the second nitrosamine moiety begins to interchange the protons being oriented *syn* and *anti* to the nitroso oxygen. Upon further increasing of the temperature the N−N rotation in both NNO moieties becomes fast and they merge to two averaged peaks due to the axial and equatorial hydrogens. In the case of the 4-fluorophenyl derivative **3b** the analogous conforma-

(11) (a) Crystallization of the dinitrosamine **1b** from toluene gave a solvate (mp 128 °C dec) with one molecule of the solvent. Its structure, also solved by us, shows essentially the same geometry of the molecule as that obtained for the compound crystallized from ethanol [the N-3 displacement, as defined above, is of 0.266(5) Å]. (b) The authors have deposited experimental details concerning the crystal structure determination of **1b** and its solvate with toluene, atomic coordinates, anisotropic 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.

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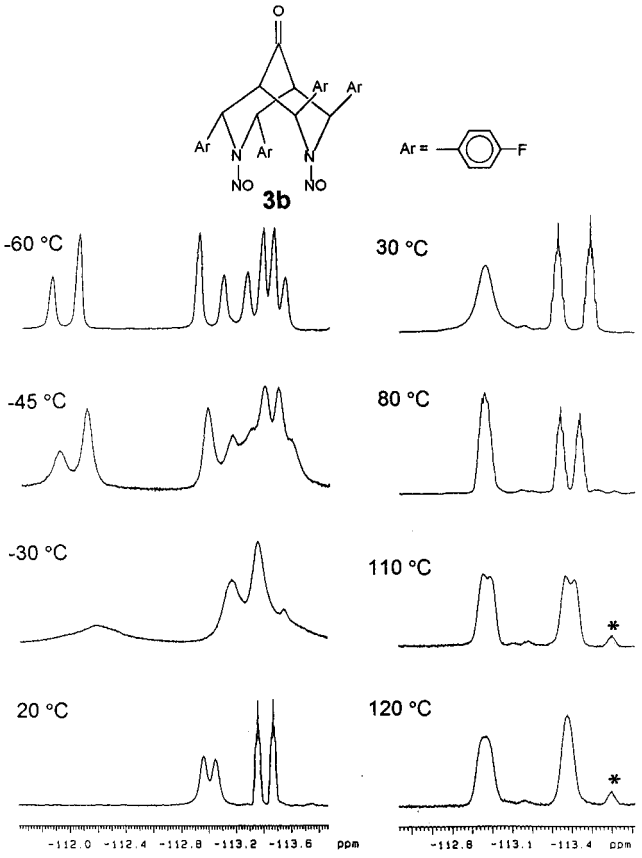

Figure 3. The variable temperature ^{19}F NMR spectra (470 MHz) of **3b** in $CDCl_3$ (left) and $C_6D_5NO_2$ (right). The signal marked by asterisk is due to a decomposition product.

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

compd	solvent	resonance of nuclei	T_c (°C)	$\Delta\nu$ (Hz)	$\Delta G^{\ddagger}$ (kcal/mol)
1b	$CDCl_3$	^1H	−30	54	12.0[b]
	$C_6D_5NO_2$	^1H	139	34	20.8
2b	$CDCl_3$	^1H	−27	62	12.1[b]
	$C_6D_5NO_2$	^1H	146	32	21.2
3b	$CDCl_3$	^1H	−39	65	11.5[b]
	$C_6D_5NO_2$	^1H	140	32	20.9
	$(CD_3)_2SO$	^1H	147	54	20.9
	$CDCl_3$	^{19}F	−34	88	11.5[b]
	$C_6D_5NO_2$	^{19}F	115	9	20.6
	$(CD_3)_2SO$	^{19}F	140	35	20.9
4b	$CDCl_3$	^1H	−2	70	13.1[b]
	$C_6D_5NO_2$	^1H	155[c]	32	21.7

[a] The errors on $\Delta G^{\ddagger}$ are ± 0.3 kcal/mol. [b] The average barier. [c] A decomposition of **4b** occurs above 150 °C.

tional interconversion process may be observed also with the aid of the variable temperature ^{19}F NMR spectra (Figure 3). Owing to their simplicity (lack of the overlapping signals), they are somewhat superior to the ^1H NMR measurements.

The free energies of activation $\Delta G^{\ddagger}$, given in Table 1, were calculated from the coalescence temperatures using Eyring equation.[17,18] Unfortunately, because of a very broad range of temperatures, each of two energy barriers to the N−N rotation had to be measured in a different solvent; i.e., $CDCl_3$ and nitrobenzene-d_5 (also DMSO-d_6 in the case of **3b**) were used below and above the room temperature, respectively. As a consequence of a significant distortion of one nitrosamine group from planarity the corresponding rotation barrier is extremely low (11.5−13.1 kcal/mol), the lowest, in fact, so far reported for *N*-nitrosopiperidine derivatives[16b] (cf., *N*-nitroso-*cis*-2,6-diphenylpiperidine 18.1 kcal/mol,[19a] *N*-nitrosobis(1-adamantyl)amine 18.0 kcal/mol,[16b] *N*-nitroso-5-azabicyclo-[2.2.1]heptane 16.5 kcal/mol,[19b] and *N*-nitroso-1,5-dimethyl-2,4-bis(2-fluorophenyl)-3-azabicyclo[3.3.1]nonan-9-one 12.2 kcal/mol[10a]). On the other hand, the second barrier height (ca. 21 kcal/mol), corresponding to the N−N rotation in the planar nitrosamine group, is close to the value reported for simple *N*-nitrosamines.

Experimental Section

Caution: All nitrosamines are potential chemical carcinogens, and special care should be taken in the handling and disposal of these substances.[20]

All spectroscopic measurements were carried out as described previously.[10a] The amines **1a**−**4a** were prepared according to the literature procedures.[6]

2,4,6,8-Tetraphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one (1a). Mp 248−250 °C (lit.[6a] mp 253−254 °C); ^1H NMR ($CDCl_3$) δ 7.58 (m, 5 H), 7.16 (m, 5 H), 6.80 (m, 5 H, 6.72 (m, 5 H), 4.66 (d, J = 2.9 Hz, 2 H), 4.37 (s, 2 H), 2.81 (m, 2 H), 2.11 (br s, 1 H), 1.57 (br s, 1 H).

2,4,6,8-Tetrakis(4-methylphenyl)-3,7-diazabicyclo[3.3.1]-nonan-9-one (2a). Mp 220−221 °C (lit.[6a] mp 245−246 °C); ^1H NMR ($CDCl_3$) δ 7.46 (d, J = 8.0 Hz, 4 H), 7.21 (d, J = 7.9 Hz, 4 H), 6.85 (d, J = 8.9 Hz, 4 H), 6.59 (d, J = 7.9 Hz, 4 H), 4.67 (d, J = 3.0 Hz, 2 H), 4.30 (s, 2 H), 2.82 (m, 2 H), 2.40 (s, 6 H), 2.21 (s, 6 H), 2.15 (br s, 1 H), 1.39 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 211.9, 142.7, 137.6, 137.2, 136.3, 129.2, 128.7, 126.5, 126.2, 63.2, 61.9, 58.2, 21.1, 21.0.

2,4,6,8-Tetrakis(4-fluorophenyl)-3,7-diazabicyclo[3.3.1]-nonan-9-one (3a). Mp 228−230 °C; ^1H NMR ($CDCl_3$) δ 7.54 (m, 4 H), 7,16 (m, 4 H), 6.74 (m, 8 H), 4.62 (d, J = 2.9 Hz, 2 H), 4.34 (s, 2 H), 2.78 (m, 2 H), 2.09 (br s, 1 H), 1.45 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 210.4, 162.3 (d, J_{CF} = 246.1 Hz), 161.8 (d, J_{CF} = 245.8 Hz), 159.8, 159.4, 128.0 (d, J_{CF} = 9.0 Hz), 127.8 (d, J_{CF} = 9.0 Hz), 115.6 (d, J_{CF} = 21.8 Hz), 115.2 (d, J_{CF} = 21.4 Hz), 62.5, 61.5, 58.0; ^{19}F NMR ($CDCl_3$) δ −114.4 (m, 2 F), −115.5 (m, 2 F). Anal. Calcd for $C_{31}H_{24}N_2OF_4$ (518.5): C, 72.08; H, 4.68; N, 5.42. Found: C, 72.03; H, 4.68; N, 5.21.

2,4,6,8-Tetraphenyl-3,7-diazabicyclo[3.3.1]nonane (4a). Mp 252−254 °C (lit.[6a] mp 268−269 °C; ^1H NMR ($CDCl_3$) δ 7.58 (m, 4 H), 7.45−7.30 (complex m, 6 H), 7.05 (m, 6 H), 6.70 (m, 4 H), 4.20 (s, 2 H), 4.12 (d, J = 2.8 Hz, 2 H), 2.78 (dt, J = 4.2 and 12.3 Hz, 1 H), 2.16 (m, 2 H), 1.84 (br s, 1 H), 1.67 (dt, J = 2.5 and 12.3 Hz), 1.30 (br s, 1 H); ^{13}C NMR ($CDCl_3$) δ 148.6, 143.5, 128.3, 127.9, 127.0, 126.1, 129.9, 63.6, 54.8, 42.4, 27.4.

***N,N′*-Dinitroso-2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]-nonan-9-one (1b).** To a suspension of amine **1a** (0.88 g, 2 mmol) in chloroform (10 mL) was added 20% hydrochloric acid (2.0 mL), and while stirring solid $NaNO_2$ (0.55 g, 8 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 Na_2SO_4. After evaporation of the chloroform the residue was crystallized from ethanol: yield 0.55 g (55%); mp 168 °C dec (from EtOH); ^1H NMR ($CDCl_3$) δ 7.50−7.20 (complex m, 10 H), 6.90−6.65 (complex m, 10 H), 6.66 (s, 1 H), 6.25 (s, 1 H), 5.62 (d, J = 5.7 Hz, 1 H), 5.57 (d, J = 5.5 Hz, 1 H), 3.86 (dt, J = 1.7 and 6.0 Hz, 1 H), 3.62 (dt, J = 1.8

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and 5.4 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 208.6, 137.8, 136.5, 136.4, 136.3, 135.9, 129.3, 129.2, 129.0, 128.6, 128.5, 128.2, 128.1, 128.0, 127.9, 127.6, 127.3, 126.7, 69.0, 67.9, 62.2, 53.9, 52.5, 52.0; UV (cyclohexane−dioxane, 4:1) λ_{max} 386 (ϵ 84), 410 nm (80). Anal. Calcd for $C_{31}H_{26}N_4O_3$ (502): C, 74.09; H, 5.21; N, 11.15. Found: C, 74.10; H, 5.17; N, 10.91.

***N,N′*-Dinitroso-2,4,6,8-tetrakis(4-methylphenyl)-3,7-diazabicyclo[3.3.1]nonan-9-one (2b)** was obtained from amine **2a** in a manner similar to that of compound **1b**: mp 165−166 °C dec (from toluene−hexane); ^{1}H NMR ($CDCl_3$) δ 7.24 (complex m, 8 H), 6.85 (m, 1 H), 6.50−6.70 (complex m, 8 H), 6.18 (s, 1 H), 5.55 (d, J = 5.9 Hz, 1 H), 5.50 (d, J = 5.2 Hz, 1 H), 3.77 (dt, J = 1.7 and 5.2 Hz, 1 H), 3.51 (dt, J = 1.6 and 5.3 Hz, 1 H), 2.39 (s, 3 H), 2.37 (s, 3 H), 2.10 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 209.1, 138.3, 138.2, 137.5, 137.2, 133.8, 133,3, 132.9, 129.9, 129.8, 128.6, 128.4, 127.2, 126.6, 126.5, 125.9, 69.1, 67.9, 62.0, 54.2, 52.7, 51.9, 21.2, 20.7; UV (cyclohexane−dioxane, 4:1) λ_{max} 386 (ϵ 92), 412 nm (90). Anal. Calcd for $C_{35}H_{34}N_4O_3$ (558): C, 75.25; H, 6.13; N, 10.03. Found: C, 75.14; H, 6.25; N, 9.92.

***N,N′*-Dinitroso-2,4,6,8-tetrakis(4-fluorophenyl)-3,7-diazabicyclo[3.3.1]nonan-9-one (3b)** was obtained from amine **3a** in a similar manner to that of compound **1b**: mp 183−185 °C (from toluene−hexane); ^{1}H NMR ($CDCl_3$) δ 7.22 (m, 10 H), 6.84 (m, 2 H), 6.60 (m, 5 H), 6.18 (s, 1 H), 5.55 (d, J = 5.9 Hz, 1 H), 5.50 (d, J = 5.2 Hz, 1 H), 3.77 (d, J = 5.9 Hz, 1 H), 3.51 (d, J = 5.3 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 208.0, 162.5 (d, J_{CF} = 248.8 Hz), 162.4 (d, J_{CF} = 248.4 Hz), 162.1 (d, J_{CF} = 249.8 Hz), 161.8 (d, J_{CF} = 249.4 Hz), 132.2 (d, J_{CF} = 3.5 Hz), 131.9 (d, J_{CF} = 3.5 Hz), 131.7 (d, J_{CF} = 3.5 Hz), 131.3 (d, J_{CF} = 3.5 Hz), 129.1 (d, J_{CF} = 8.2 Hz), 128.5 (d, J_{CF} = 8.4 Hz), 128.3 (d, J_{CF} = 8.2 Hz), 127.7 (d, J_{CF} = 8.3 Hz), 116.5 (d, J_{CF} = 22.0 Hz), 116.4 (d, J_{CF} = 22.0 Hz), 115.2 (d, J_{CF} = 21.8 Hz), 115.0 (d, J_{CF} = 21,5 Hz), 68.2, 67.1, 61.5, 54.0, 52.6, 51.0; ^{19}F NMR ($CDCl_3$) δ −112.8 (m, 1 F), −112.9 (m, 1F), 113.2 (m, 1 F), −113.3 (m, 1 F); UV (cyclohexane−dioxane, 4:1) λ_{max} 386 (ϵ 79), 414 nm (79). Anal. Calcd for $C_{31}H_{22}N_4O_3F_4$ (576.5): C, 64.58; H, 4.20; N, 9.72. Found: C, 64.36; H, 4.18; N, 9.59.

***N,N′*-Dinitroso-2,4,6,8-tetraphenyl-3,7-diazabicyclo[3.3.1]-nonane (4b)** was obtained from amine **4a** in a manner similar to that of compound **1b**: mp 194−195 °C dec; ^{1}H NMR ($CDCl_3$) δ 7.5 −7.35 (complex m, 18 H), 6.55 (m, 2 H), 6.11 (br s, 1 H), 5.94 (br s, 1 H), 5.41 (br s, 1 H), 5.31 (br s, 1 H), 3.32 (m, 1 H), 3.04 (m, 2 H), 2.28 (m, 1 H); ^{13}C NMR ($CDCl_3$) δ 138.7, 138.5, 138.2, 137.2, 129.1, 128.9, 128.2, 128.0, 127.8, 127.7, 127.6, 127.1, 127.0, 126.8, 125.9, 125.3, 59.3, 50.6, 38.2, 35.8, 23.9; UV (cyclohexane−dioxane, 4:1) λ_{max} 384 (ϵ 79), 404 nm (107). Anal. Calcd for $C_{31}H_{28}N_4O_2$ (488): C, 76.21; H, 5.78; N, 11.47. Found: C, 76.30; H, 5.80; N, 11.29.

X-ray Diffraction Analysis. Unit-cell parameters and intensity data for **1b** and **1b**·toluene have been measured on a Kuma KM-4 diffractometer. The data were corrected for Lorentz and polarization factors but not for absorption. Crystal data for $C_{31}H_{26}N_4O_3$ (**1b**): monoclinic, space group $P2_1/c$, a = 11.403(2), b = 13.875(3), c = 31.948(6) Å, β = 90.53(3)°, V = 5055(2) Å^3, Z = 8, D_{calcd} = 1.321 g cm^{-3}, λ(Cu Kα) = 1.54178 Å, T = 293 K, R_1 = 0.043, wR_2 = 0.118 for 5709 reflections with $I > 2\sigma(I)$. Both nitroso groups exhibit disorder. During refinement the unit occupancy of each NO group was split into two fractions, and constraints were imposed on interatomic 1,2 and 1,3 distances within the N−N═O fragments. The occupancies of higher populated conformers are of 0.807(6) and 0.794(5) in the molecule A, and 0.798(6) and 0.633(6) in the molecule B for the N3−NO and N7−NO groups, respectively. Crystal data for $C_{31}H_{26}N_4O_3{\cdot}C_7H_8$ (**1b**·toluene): monoclinic, space group $P2_1/c$, a = 16.710(5), b = 8.921(2), c = 22.073(8) Å, β = 106.71(3)°, = 3152(2) Å^3, Z = 4, D_{calcd} = 1.253 g cm^{-3}, λ(Mo Kα) = 0.71073 Å, T = 293 K, R_1 = 0.086, wR_2 = 0.245 for 2349 reflections with $I > 2\sigma(I)$. The NO groups exhibit disorder and they were treated analogously as in **1b** in the refinement process. Some constraints were also imposed on the 1,2 and 1,3 distances and planarity of the solvent molecule. The occupancies of higher populated conformers are 0.93(1) and 0.60(2) for the N3−NO and N7−NO groups, respectively. Different occupancies of the higher populated rotamers in the molecule B of **1b** and **1b**·toluene indicate that the *syn* and *anti* stereoisomers have to occupy the same site in the crystal. In the case of the molecule A of **1b** both enantiomeric *anti* conformers as well as a mixture of the *syn* and *anti* forms can give similar patterns of disorder.

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Supporting Information Available: The ORTEP drawing of the X-ray structure and crystal packing of **1b**·toluene, variable temperature ^{1}H NMR spectra of **2b**, and the UV-vis spectra of **1b** and related *N*-nitrosamines (4 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.

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