Synthesis and NMR Investigation of 3,4-Diazabicyclo[4.3.0]non-2-ene and *N,N'*-Azo-3-azabicyclo[3.3.0]octane. X-ray Crystal Structure Analysis of a New Tetrazene Derivative

H. Delalu*, M. Elkhatib and L. Peyrot

Laboratoire de Physico-Chimie Minérale 2, UPRES A CNRS 5079, Université Claude Bernard Lyon I,
Bâtiment 731, 43 Boulevard du 11 novembre 1918, 69622 Villeubanne cedex, France

B. Fenet

Centre RMN, UPRES A 5012, Université Claude Bernard Lyon I - CPE, Bâtiment 308,
43 Boulevard du 11 novembre 1918, 69622 Villeurbanne cedex, France

B. F. Mentzen

Laboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Université Claude Bernard Lyon I,
Bâtiment 731, 43 Boulevard du 11 novembre 1918, 69622 Villeurbanne cedex, France

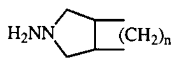
Received September 29, 1997

3,4-Diazabicyclo[4.3.0]non-2-ene and *N,N'*-azo-3-azabicyclo[3.3.0]octane are the main products of the oxidation of *N*-amino-3-azabicyclo[3.3.0]octane by chloramine. These new compounds have been isolated and characterized. A structural study has been performed with the goal of establishing the *cis-trans* configuration at the bicyclic junction. Multinuclear proton decoupling carried out on the endocyclic hydrazone has allowed the determination of the coupling constant of the bridgehead hydrogens. A low temperature conformational study shows splitting of the ^{13}C signal of the carbon atom located α with respect to the ammonia nitrogen. This result, consistent with a *cis* structure, was confirmed by a nmr analysis conducted on the solid tetrazene derivative. The X-ray data collection on a single cyrstal of the tetrazene has permitted us to determine the crystallographic properties of this compound. Data processing by direct methods reveals that the geometry of the molecule presents a *cis* configuration for the bicyclic bridge link and a *trans* one for the azo group, confirming thus the main results obtained by nmr studies.

J. Heterocyclic Chem., **36**, 681 (1999).

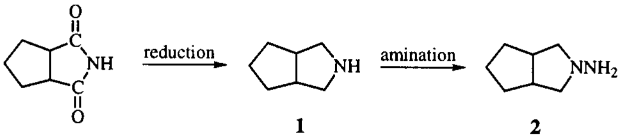
Introduction.

Asymmetric alicyclic hydrazines described by the formula:



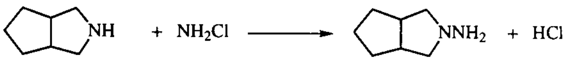
(n = 1, 2, 3),

are used as precursors of hypoglycemic and antihypertensive medicines [1]. Their synthesis consists of several steps of which the first corresponds to a cyclization reaction involving the action of ammonia on 1,2-cyclopentane dicarboxylic acid (n = 3):

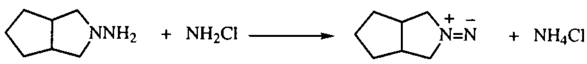


1 2

This study relates to *N*-amino-3-azabicyclo[3.3.0]octane **2**, which is used for the synthesis of *glyclazide*, the active principle destined for the treatment of non-insulin dependent diabetics. During amination (1), several products are observed which mainly result from the oxidation of hydrazine by chloramine (2):

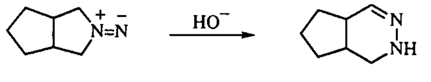


(1)

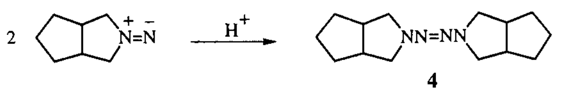


(2)

Depending to the *p*H value [2], the aminonitrene formed undergoes an intramolecular rearrangement (3) or a dimerization (4) leading to endocyclic hydrazone **3** or tetrazene **4**, respectively.



3 (3)



4

(4)

This reactive chain results in an uncertainty concerning the configuration of the bridgehead hydrogens, which remains unchanged in the course of the later steps leading to hydrazine. Literature indicates a *cis* configuration for the corresponding hydrocarbon, bicyclo[3.3.0]octane [3]. However, this fact is insufficient to provide the structure of **1** given the difference in the methods of preparation of these products. With the goal to determine the *cis-trans* configuration, the new compounds were the object of a preliminary characterization completed by an X-ray and nmr investigation centered around the protons adjacent to the bridgehead.

Results and Discussion.

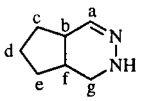
I. Synthesis and Characterization of 3,4-Diazabicyclo-[4.3.0]non-2-ene and *N*,*N*'-Azo-3-azabicyclo[3.3.0]octane.

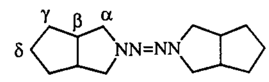
Oxidation of *N*-amino-3-azabicyclo[3.3.0]octane by monochloramine at *p*H = 12.89 under stoichiometric conditions (T = 25°) shows the formation of compound **3**. Gas chromatography and gc/ms analysis indicate the formation of a single product, which is attributed this to a M^+ peak at m/z = 124. An isotopic study of the ions fragments lead to an empirical formula $C_7H_{12}N_2$. Elemental analysis of the pure product (99.2% gc) shows good agreement between the experimental and calculated percentages. Infrared spectrum of **3** presents two intense bands at 1620 and 3320 cm^{-1} which correspond to the C=N and N-H bond stretchings, respectively. Interpretation of the cross-peaks in the two dimensional $^{13}C/^{1}H$ nmr spectrum is consistent with the above formula. Discrimination between CH_2 and CH carbons was accomplished by the standard DEPT sequence [4]. The ultraviolet spectrum exhibits a strong absorption at λ = 229 nm with a molar extinction coefficient of ε = 2685 M^{-1} cm^{-1}. The spectral data are given in the Experimental.

The relative acidification of the solution induces a decrease in the formation of **3** in favor of **4**, which precipitates and becomes preponderant in the neighborhood of *p*H ≈ 9. The purity of the product determined by elemental analysis confirms the established empirical formula $C_{14}H_{24}N_4$. The mass spectrum was performed using a hexane solution with the electron impact source at 70 eV. The presence of a molecular peak and of an ion fragment situated at m/z 248 and 110, respectively, are consistent with the formula developed above. The m/z = 110 peak corresponds to the formation of two $C_7H_{12}N^{\bullet +}$ moieties with liberation of a dinitrogen molecule. DEPT and 2D $^{13}C/^{1}H$ nmr spectra show four carbon signals which are slightly more deshielded than in **1**. These results associated with the ir analysis prove the existence of symmetry in the molecule and exclude a simple dimerization of **3**. The uv spectrum was measured in hexane because of the low solubility of the compound in water. It shows an absorption band at λ_1 = 280 nm (ε_1 = 11900 M^{-1} cm^{-1}) and a shoulder at λ_2 = 285 nm (ε_2 = 11900 M^{-1} cm^{-1}) characteristic of a tetrazene-type structure. The synthesis procedure and the spectral data are given in the Experimental.

II. NMR Investigation of 3,4-Diazabicyclo[4.3.0]non-2-ene and *N*,*N*'-Azo-3-azabicyclo[3.3.0]octane.

A ^{13}C and ^{1}H nmr study of **1** and **2** have not led to a conclusive determination of the configuration. The problem is tied to the symmetry observed in these compounds and to the multiple short and long-distance ^{1}H homonuclear couplings due to the saturated carbon chain. However, the exploitation of nmr spectra related to oxidation products is more reasonable of the dissymmetrical structure and the resonance effect observed in **3** and **4**, respectively.





Structural Study of 3,4-Diazabicyclo[4.3.0]non-2-ene.

Cross-peaks in the two dimensional $^{13}C/^{1}H$ nmr spectrum allows the assignment of protons relatively to the corresponding carbons. One can observe that signals H_b and H_f constitute a complex multiplet (3.35 ppm) to which is added one of the two protons H_g and the direct interpretation of the spectrum turns out to be impossible (Figure 1). Complementary runs at several temperatures (-105 to 28°) and in different solvents (pyridine, benzene, mixture) did not allow the differentiation of the protons in question.

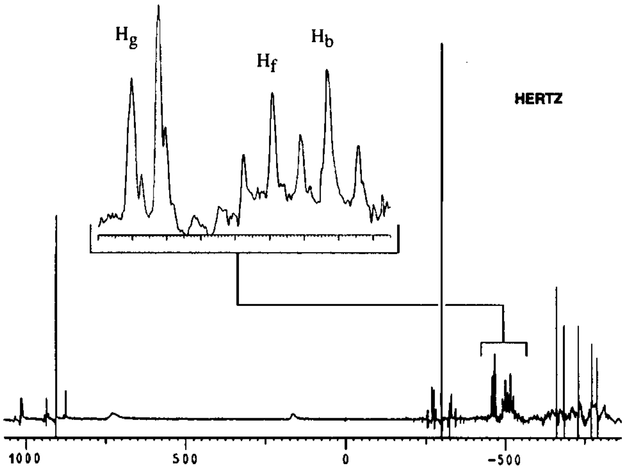


Figure 1. Multisite homonuclear spin decoupling spectrum of 3,4-diazabicyclo[4.3.0]non-2-ene: reduction of the multiplet to the only reciprocal interactions H_b, H_f and H_g.

In order to reduce the multiplet at 3.35 ppm to the only reciprocal interactions between H_b, H_f, and H_g, a multisite homonuclear decoupling experiment was performed. Upon the simultaneous decoupling of H_a, H_g, H_c, H_d, H_e, H'_g, the spectrum obtained exhibits two doublets and a triplet due to the coupling between the three different protons described above (Figure 1). One can see distortions in intensity and a slight deformation caused by second order effects but coupling constant can be extracted.

Analysis of the signals leads to $J_{H_bH_f}$ = 8.9 Hz and $J_{H_fH_g}$ = 7.9 Hz but does not allow definite assignment of H_b and H_f. On the other hand, a calculated spatial representation (Figure 2) of the *cis* and *trans* forms leads to dihedral angles (H_b-C_b-C_f-H_f) on the order of 4 and 165 degrees, respectively. One can deduce the corresponding coupling constants J_{cis} = 8.2 Hz and J_{trans} = 8.6 Hz. These data, consistent with the experimental value ($J_{H_bH_f}$ = 8.9 Hz), are nonetheless too close to decide between the two configurations.

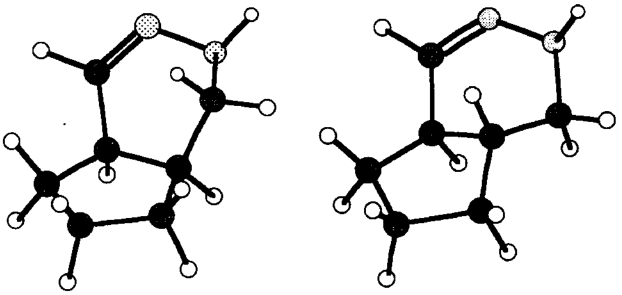


Figure 2. Theorectical spatial representation of the *cis* and *trans* forms of 3,4-diazabicyclo[4.3.0]non-2-ene.

A conformational study bearing upon the two configurations reveals greater flexibility of the *cis* form compared to the *trans* form. This property results in a seesaw motion of carbon g around the plane of the heterocycle. In consequence, a slowing of the inversion rate should cause splitting of the ^{13}C signal of that atom. This is indeed what is observed when the spectra were recorded at -105° in deuterated dichloromethane (Figure 3). This result supports the *cis* structure but remains insufficient for a definite determination.

Structural Study of *N,N'*-Azo-3-azabicyclo[3.3.0]octane: NMR Approach.

A 75 MHz ^{13}C nmr analysis in deuteriochloroform shows four resonances situated at 57.1 (C_α), 40.2 (C_β), 33.3 (C_γ), and 26.1 (C_δ) ppm. Discrimination between the nuclei of even and odd multiplicities was achieved by using a DEPT 135 pulse sequence. The three first peaks each correspond to four equivalent atoms while the most shielded resonance represents the two terminal carbons.

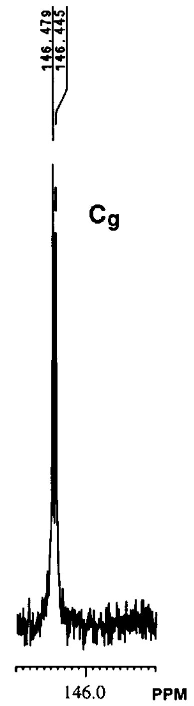


Figure 3. ^{13}C nmr spectrum of **3** in deuterated dichloromethane at -150°: splitting of the C_g signal.

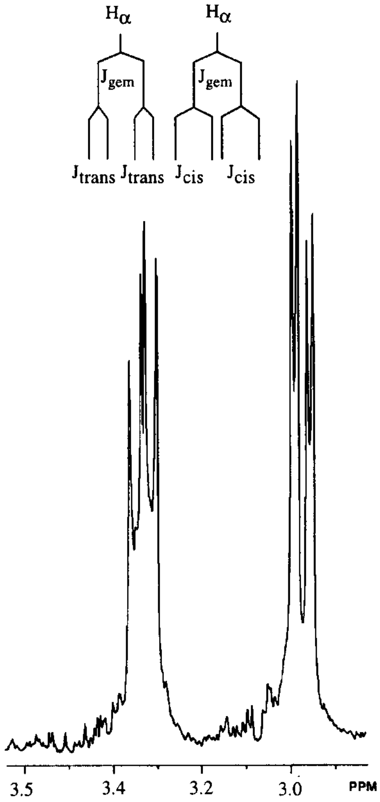


Figure 5. *N,N'*-azo-3-azabicyclo[3.3.0]octane ^1H nmr resonances of the geminal protons ($H\alpha$ and $H'\alpha$) in deuteriochloroform: determination of the *cis* configuration coupling constant of the bridgehead hydrogens.

This pattern confirms the existence of a global symmetry element with respect to the carbon chain of the molecule. One can note a shift of + 3 ppm of the C_α with respect to that of **1** caused by the electron-withdrawing effect of the sp^2 nitrogen and the resonance effect.

Exploitation of the $^{13}C/^{1}H$ two-dimensional spectrum (Figure 4) shows that the geminal protons H_α and H'_α are not magnetically equivalent and their chemical shifts are located at 3 and 3.3 ppm. In each fragment of the tetrazene, the α proton is coupled with its geminal homologue (H'_α) and vicinal proton (H_β), which corresponds to an AMX system.

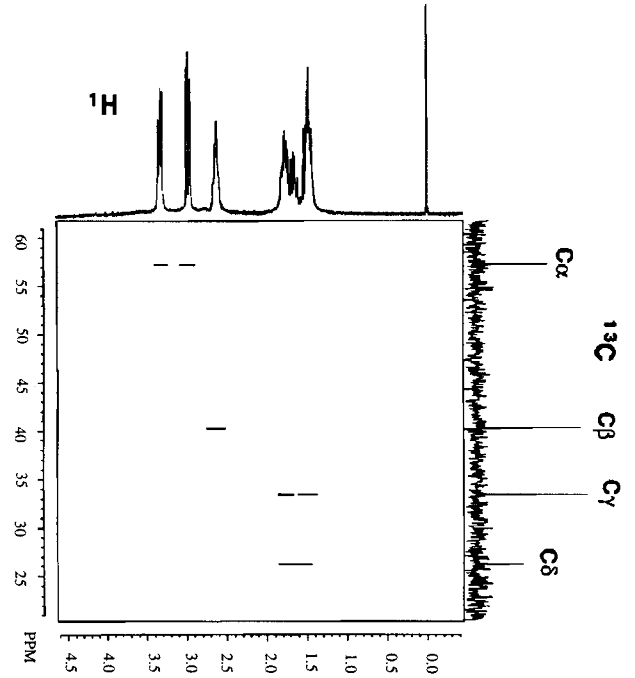


Figure 4. 2D $^{13}C/^{1}H$ spectrum of *N,N'*-azo-3-azabicyclo[3.3.0]octane in deuteriochloroform.

Theoretically, in the case of a *cis* structure, the nmr lines corresponding to the α protons oriented towards the same side of the heterocyclic plane are overlapping and the spectrum reduces to two quadruplets. In the opposite case, one of the above protons is coupled with a *cis* H_β while the second is coupled with a *trans* H_β. This should cause a degenerescence of the lines and the formation of two octuplets. In reality, one can see two resonances that are split twice, first by the J_{gem} coupling, second by the J_{cis} or J_{trans} coupling. Figure 5 presents the ^1H nmr spectra of the geminal protons and the associated coupling diagram from which one can deduce a *cis* structure with the following shifts:

J_{gem} (H_α,H'_α) = 10.19 Hz; J_{cis} (H_α,H_β) = 7.86 Hz; J_{trans} (H'_α,H_β) = 3.87 Hz

The coupling constants are compatible with those obtained from the theoretical dihedral angles and prove clearly the *cis* configuration of 3-aza-bicyclo[3.3.0]octane derivatives. In hope of confirming this result and taking account of the numerous possible isomers of **4**, a single-crystal X-ray diffraction study was undertaken.

Structural Study of *N,N'*-Azo-3-azabicyclo[3.3.0]octane: X-ray Approach.

A structural investigation on a single-crystal of rather low quality enabled us to determine the geometry of the tetrazene. Only carbon atoms could be localized. After several selective recrystallizations of **4** in water-ethanol solutions, some morphologically and mechanically suitable single-crystals were obtained. The results concerning the structural study and the interpretation of the X-ray data collection corresponding to **4** are reported in the Experimental. The unit-cell contains one centro-symmetrical $C_{14}H_{24}N_4$ formula unit. Structure analysis by direct methods reveals the geometry of the molecule. Thus, the tetrazene (Figure 6) presents an inversion center situated on the N_1-N_1* bond of the N_4 bridge. For clarity, only the H_β type hydrogen atoms corresponding to the C_2-C_6 bridge are represented.

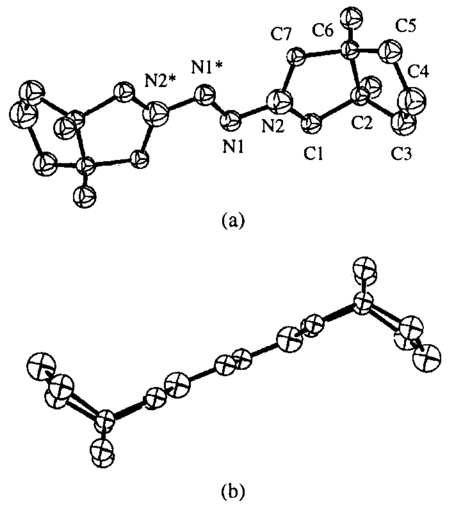


Figure 6. Molecular structure of *N,N'*-azo-3-azabicyclo[3.3.0]octane: two ORTEP-III [10] illustrations of **4** showing the C, N atoms numbering system. Only the hydrogen atoms in the *cis* configuration (H_β type) corresponding to the C_2-C_6 bridge are shown. (a) best view; (b) view through the N_4 bridging plane N_2-N_1-N_1*-N_2*.

Figure 6 clearly shows the *cis* configuration of these H_β in the $C_7H_{12}N_2$ asymmetric moiety of the tetrazene. The refined fractionnal atomic coordinates corresponding to all the C, N atoms are given in Table 1.

Table 1

Positional and Isotropic Thermal Parameters of C, N Atoms

Atom [a]	X	Y	Z	B(Å2)
N1	0.9104(6)	0.1028(5)	0.9888(3)	6.01(8)
N2	0.7666(7)	0.1029(6)	0.8998(3)	9.20(9)
C1	0.5447(7)	0.3125(6)	0.8706(3)	5.81(9)
C2	0.4236(6)	0.2629(6)	0.7750(3)	4.97(8)
C3	0.482(1)	0.3784(7)	0.6696(3)	8.8(1)
C4	0.697(1)	0.1914(9)	0.6092(4)	11.2(2)
C5	0.705(1)	-0.0416(7)	0.6493(3)	7.9(1)
C6	0.5807(6)	-0.0133(5)	0.7634(3)	4.91(8)
C7	0.8027(7)	-0.1045(5)	0.8488(3)	4.86(8)

[a] All atoms were refined isotropically.

Some selected bond lengths and angles are summarized in Table 2. The H_2-C_2-C_6-H_6 dihedral angle (6.5°) is in excellent agreement with the value calculated (11.9°) by using the experimentally determined nmr coupling constant (J_{cis} = 7.86 Hz).

Table 2

Main Bond Angles and Bond Distances X-ray Assignments for *N*,*N*'-Azo-3-azabicyclo[3.3.0]octane

Bond Angles in Degrees [a]		Bond Distances in Angstroms [a]	
N1-N2-C1	117.2(3)	N1-N2	1.384(5)
N1-N2-C7	124.8(3)	N2-C1	1.353(4)
N2-C1-C2	106.6(3)	N2-C7	1.397(5)
N2-C7-C6	104.8(3)	C1-C2	1.498(5)
C1-N2-C7	117.2(4)	C2-C3	1.504(6)
C1-C2-C3	115.4(3)	C2-C6	1.543(4)
C1-C2-C6	105.2(2)	C3-C4	1.434(6)
C2-C3-C4	108.0(3)	C4-C5	1.439(7)
C2-C6-C5	105.7(2)	C5-C6	1.512(5)
C2-C6-C7	105.2(2)	C6-C7	1.521(5)
C3-C2-C6	105.2(2)		
C3-C4-C5	109.6(5)		
C4-C5-C6	106.7(3)		
C5-C6-C7	114.7(3)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

EXPERIMENTAL

Nuclear magnetic resonance analysis were obtained with a high resolution Bruker AM 300 spectrometer at 300 MHz for ^1H and 75 MHz for ^{13}C. All nmr spectra were recorded in deuteriochloroform solution. Chemical shifts are given in δ values (ppm) against tetramethylsilane as the internal standard. The multisite homonuclear decoupling was realized with a homemade accessory. The pure homonuclear frequency was picked at the output of the spectrometer, phase modulated by the console and amplitude modulated with a wave form generated by a PC computer, amplified and finally reinjected to the probe by the decoupler channel. No definitive changes of the spectrometer were necessary, and any number of decoupling frequencies were possible. The $^{13}C/^1H$ 2D correlation used the standard Bruker XH CORR. AU microprogram. The parameters were: SI2 = 2048, SW2 = 3125 Hz, NE = 256, SW1 = 1528 Hz, NS = 4. Data are represented in the module mode.

Infrared spectra were measured with a Beckman 842 instrument with CsI cells. The X-ray data were collected with a CAD4 four-circle diffractometer (Enraf Nonius). Ultraviolet spectra were obtained with a Cary 1E double beam spectrophotometer with 1 cm pathlength quartz cells. Gas chromatography analysis were carried out on a HP 5890 chromatograph equipped with FID and TCD detectors. Chromatograms were recorded after extraction with hexane using toluene as reference. The column (inox, 150 cm x 0.2 cm i.d.) was packed with 28% Pennwalt 223 + 4% KOH on gas chrom R. Coupled gc/ms spectra were performed in a Delsi Nermag mass spectrometer with a BP 20 capillar column (50 m) and an ion source of 70 eV. Thermodynamics data have been determined using a differential scanning calorimeter 111 Setaram.

Monochloramine.

Monochloramine is unstable in water, so it was prepared at -10°, immediately before use, by reacting 25 ml of 2.14 *M* sodium hypochlorite and 20 ml of an aqueous ammonia-ammonium chloride solution (3.6 *M* ammonia; 2.3 *M* ammonium chloride) in the presence of diethyl ether (40 ml) [5]. The organic layer was shaken and washed several times with aliquots of distilled water. Monochloroamine in aqueous solution was obtained by re-extraction from the ethereal phase. Its content was determined by uv absorption at λ = 243 nm (ε = 458 M^{-1} cm^{-1}).

3-Azabicyclo[3.3.0]octane **1**.

3-Azabicyclo[3.3.0]octane **1** is not commercially available. It was prepared from an acidic solution of amine sulfate (16%). After neutralization, the mixture was distilled at 760 torr. The first fraction was a heteroazeotropic solution (bp = 98.4°) 29.8% in **1**. Treatment with sodium hydroxide followed by redistillation yields 99.9% 3-azabicyclo[3.3.0]octane. The major impurities detected by gc are essentially water and *N*-amino-3-azabicyclo-[3.3.0]octane.

N-Amino-3-azabicyclo[3.3.0]octane **2**.

N-Amino-3-azabicyclo[3.3.0]octane **2** was produced continuously in biphasic solution in a cylindrical reaction vessel vigorously agitated by a coaxial overhead stirrer equipped with perpendicular blades in order to keep the mixture in emulsion [6]. A 1 *M* solution of monochloramine (2 l), 3-azabicyclo[3.3.0]octane (3.8 l of a 29.8% aqueous solution) and 6 *M* sodium hydroxide (0.5 l) were simultaneously introduced using a 5-fold excess of amine over haloamine and the *p*H fixed at 13.4. The reaction temperature was maintained around 60°. A mixture with about 0.26 *M* hydrazine was obtained (yield = 82%). After elimination of the ammonia, the reaction solution was distilled at atmospheric pressure to separate the 3-azabicyclo[3.3.0]octane in the form of a heteroazeotrope. The hydrazine was then isolated by addition of sodium hydroxide, then redistilled under the vacuum of a mechanical pump. The total yield reaches 72% (182 g) and the final purity is around 99.8% by gc. Compound **2** was analysed directly by gc or uv after reaction with an excess of formaldehyde in a buffered solution at *p*H = 6.9. The absorbance of the resulting hydrazone was measured at 237 nm (ε = 5352 ± 20 M^{-1} cm^{-1}) [7].

3,4-Diazabicyclo[4.3.0]non-2-ene **3**.

3,4-Diazabicyclo[4.3.0]non-2-ene **3** was prepared at 25° by adding monochloroamine (1 l, 0.5 *M* to an alkaline solution of

N-amino-3-azabicyclo[3.3.0]octane in 0.75 *M* sodium hydroxide). The reaction is instantaneous and upon addition of sodium hydroxide, the reaction mixture separates. The organic phase is distilled at a pressure of under 1 mm Hg. In the head of the column, one obtains the residual hydrazine **2** followed by **3** which condenses at 37-38° (39 g). Its purity is close to 99.2% by gc; ir: ν 3320 (NH), 2800-3000 (broad), 1620 (C=N), 1440-1480, 1310, 1090, and 720 cm^{-1} ; uv: λ_{max} = 229 nm (ε = 2685 M^{-1} cm^{-1}); ^1H nmr (deuteriochloroform): δ 6.88 (d, 1H, H_a), 3.07-3.03 (m, 1H, H_g), 2.48-2.31 (m, 1H, H_g), 2.48-2.31 (m, 2H, H_b-H_f), 1.99-1.70 (m, 2H, H_e-H_c), 1.56-1.36 (m, 2H, H_e-H_c), 1.67-1.36 (m, 2H, H_d); ^{13}C nmr (deuteriochloroform): δ 23.2 (C_d), 29.2 (C_c), 30.5 (C_e), 34.4 (C_b), 35.9 (C_f), 45.3 (C_g), 144.4 (C_a); ms: (70 eV) m/z 124 (M^+, 100 %), 123 (40), 95 (23.3), 94 (10.6), 83 (28), 82 (11), 81 (54), 68 (25), 67 (37), 55 (14), 41 (25), 39 (21), 30 (53.5), 28 (31).

Anal. Calcd. for $C_7H_{12}N_2$: C, 67.74; H, 9.67; N, 22.58. Found: C, 67.69; H, 9.64; N, 22.71.

N,N'-Azo-3-azabicyclo[3.3.0]octane **4**.

N,N'-Azo-3-azabicyclo[3.3.0]octane **4** is prepared at 25° and *p*H = 8 by oxidation of *N*-amino-3-azabicyclo[3.3.0]octane under stoichiometric conditions (0.05 *M*). This reaction, which is independent of the nature of the oxidant, leads transiently to an aminonitrene which immediately dimerizes to tetrazene. The solid precipitate is filtered, washed, and dried under vacuum (0.3 g). It is then stored under nitrogen at low temperature in the dark because of its photosensitivity, mp = 74.4°, $\Delta H_f = -2 \times 10^4$ kJ mol^{-1}; ir : ν 2800-3000 (broad), 1440-1480, 1380, 1090, 720 and 560 cm^{-1} ; uv (hexane): λ_1 = 282 nm (ε_1 = 11900 M^{-1} cm^{-1}), λ_2 = 255 nm (ε_1 = 6120 M^{-1} cm^{-1}); ^1H nmr (deuteriochloroform): δ 3.35-3.29 (q, 4H, H_δ), 2.99-2.94 (q, 4H, H_δ), 2.65-2.59 (m, 4H, H_γ), 1.80-1.61 (m, 4H, H_β), 1.80-1.43 (m, 4H, H_α), 1.55-1.43 (m, 4H, H_β); ^{13}C nmr (deuteriochloroform): δ 26.1 (C_α), 33.3 (C_β), 40.2 (C_γ), 57.1 (C_δ); ms: (70 eV) m/z 248 (M^+, 60), 110 (27), 93 (14), 81 (100%), 68 (30), 67 (61), 55 (51), 54 (47), 53 (34), 44 (41), 43 (34), 42 (91.5), 41 (90), 40 (13), 39 (56), 30 (84), 29 (40), 28 (27), 27 (34).

Anal. Calcd. for $C_{14}H_{24}N_4$: C, 67.74; H, 9.67; N, 22.58. Found: C, 67.58; H, 9.74; N, 22.77.

Crystal Structure Determination of **4**.

Colorless crystals of **4** were obtained by slow evaporation of water-ethanol solutions; crystal data: $C_{14}H_{24}N_4$, *M* = 248.37, triclinic, space group $P\bar{1}$, a = 5.114 (2), b = 6.051 (1), c = 12.529 (3) Å, α = 84.79 (2), β = 85.34 (2), γ = 65.71 (2)°, U = 351.1 $Å^3$ (from the least-squares setting angles of 21 reflections; $12.62 < \theta < 23.51°$), Cu-Kα-radiation, λ = 1.5418 Å, Z = 1, D_c = 1.171 g cm^{-3}, F (000) = 136, no absorption corrections, colorless crystals; size 0.05 x 0.4 x 0.4 mm. The crystal platelets are very thin and brittle; data collection and processing: Enraf-Nonius CAD4 diffractometer at 293 K, ω-2θ scan mode, ω scan angle (2.50 + 1.20 tan)°, variable speed (4.12-8.24° min^{-1}), maximum count time 30 s, 1363 reflections measured ($3 < \theta < 65.0°$), h / ± k / ± l = 6/7/14 respectively. The intensities of three standard reflections (211, 004, $1\bar{1}\bar{1}$) were monitored every hour of X-ray exposure time and showed no significant loss of intensity. All 1363 measured reflections were unique and corrected for Lorentz and polarization effects; structure analysis and refinement: structure solution was studied by direct methods [8]. Full-matrix least-squares refinement with isotropic thermal motion was assumed for all atoms (C, N, H). Tetrazene presents an inversion center; asymmetric unit: $C_7H_{12}N_2$. At convergence R and Rw were 0.082 and 0.066 respectively, for the 131 variables refined using the 1187 data for which $I > 2\sigma(I)$. Computations were performed with SHELXS-86 [9] and SHELXL-93 programs [10] (PC versions). Additional material comprises the refined atomic coordinates and equivalent isotropic thermal parameters, bond lengths and angles corresponding to all atoms, observed and calculated structure factors for compound **4** have been deposited at the Cambridge Crystallographic Data Centre.

REFERENCES AND NOTES

[1] S. Ehrreich and L. Zitowitz, German offen. 2,415,064 (1974); *Chem. Abstr.*, **82**, 4115g (1975).

[2] M. Elkhatib, Thèse de Doctorat n°89-94, Lyon, 1994, 186 pp.

[3] A. W. Rytina, R. W. Schiessler and F. C. Whitmore, *J. Am. Chem. Soc.*, **71**, 751 (1949).

[4] D. M. Dodrell, D. T. Pegg and M. R. Bendall, *J. Magn. Reson.*, **48**, 323 (1982).

[5] R. Cohen-Adad, H. Delalu and H. Sautereau, French Demande 2,383,916 (1977); *Chem. Abstr.*, **91**, 19887V (1979).

[6] R. Cohen-Adad, A. Cohen, H. Delalu, A. Marchand and A. Maugé, S. African ZA 87 04,526 (1987); *Chem. Abstr.*, **109**, 131251z (1988).

[7] H. Delalu and A. Marchand, *Anal. Chim. Acta*, **266**, 39 (1992).

[8] G. M. Sheldrick, SHELXS-86, a program for the solution of crystal structures from diffraction data, *Acta Crystallogr.*, **A46**, 467 (1990).

[9] G. M. Sheldrick, SHELXL-93, a program for the refinement of crystal structures from diffraction data.

[10] M. N. Burnett and C. K. Johnson, ORTEP-III, Oak Ridge thermal ellipsoid plot program for crystal structure illustrations, ORNL-6895 report, PC and Apple Macintosh 1996 versions.