

**1,8-Diazabicyclo[6.6.4]octadeca-4,11,16-triyne
A Bridgehead Amine with Planar Nitrogens**

Volker Wolfart ^{a)}, Rolf Gleiter ^{a)*}, Claus Krieger ^{b)} and Hans Pritzkow ^{c)}

^{a)} Organisch-Chemisches Institut der Universität Heidelberg
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

^{b)} Abteilung Chemie des Max-Planck Instituts für Medizinische Forschung,
Jahnstraße 26, D-69120 Heidelberg, Germany

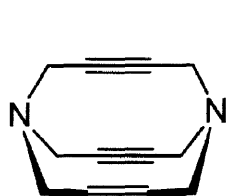
^{c)} Anorganisch-Chemisches Institut der Universität Heidelberg
Im Neuenheimer Feld 270, D-69120 Heidelberg, Germany

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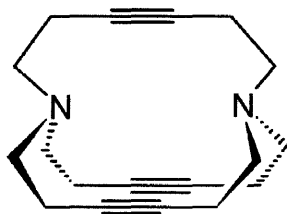
Abstract: The synthesis of 1,8-diazabicyclo[6.6.4]octadeca-4,11,16-triyne (**3**) has been achieved, X-ray investigations on single crystals reveal an almost planar conformation of the nitrogen atoms.

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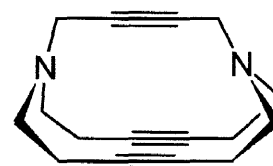
Bridgehead bicyclic amines containing medium- or large-sized rings adopt interesting structures, exhibit remarkable basicities and show intrabridgehead chemistry.¹ In the course of our studies of bridged 1,6-diazacyclodeca-3,8-diyne² and 1,8-diazacyclotetradeca-4,11-diyne³ we have obtained 1,6-diazabicyclo[4.4.4]tetradeca-3,8,12-triyne² (**1**) and 1,8-diazabicyclo[6.6.6]eicosa-4,11,17-triyne³ (**2**) by simple procedures.



1

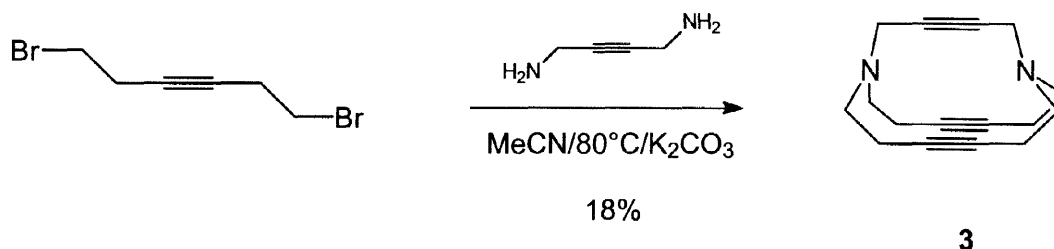


2



3

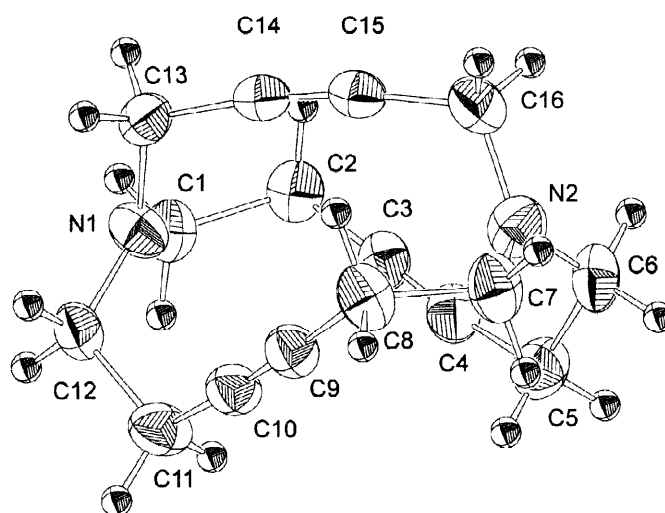
Several congeners of **1** and **2** are possible by varying the length of the bridges. In this paper we report a remarkably simple access to 1,8-diazabicyclo[6.6.4]octadeca-4,11,16-triyne (**3**) and compare its structure with that of **2**. The synthesis of **3** was achieved in a one pot procedure by reacting 1,6-dibromo-3-hexyne⁴ with 1,4-diamino-4-butyne⁵ applying high-dilution techniques.



Scheme 1

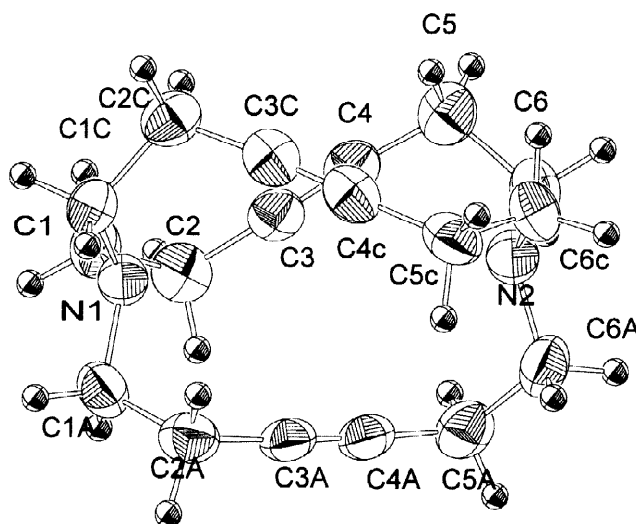
The structure of **3** has been established by spectroscopic properties⁶ and by X-ray analysis of single crystals.⁷

The X-ray structure of **3** shows almost completely flat nitrogen atoms and C-N-C bond angles average to 119.59 (2)°. The sums of the C-N-C angles are 358.71° and 358.85°, respectively. The length of the triple bonds in **3** are 1.182(3), 1.185(3) and 1.185(3) Å, thus showing little difference in the different bridges.



X-ray structure of **3**

The angles at the triple bonds of **3** are bent by 7.15° in the four-atom bridge, due to the strain in the molecule which also causes its six-atom bridges to be a bit more twisted (48.62°) against each other than in the higher symmetric triyne **2** (47.80°). The triyne **2** exemplifies a typical *in/in*-conformation and triyne **1** which has not yet been structurally fully characterized most likely possesses a stretched DABCO structure with *out*-side lone pairs. The new amine **3** with its unusual non-pyramidal nitrogens does not belong to either of the two conformer-families. The transannular nitrogen-nitrogen distances are 4.99 Å in **3** and 5.05 Å in **2**, demonstrating that the 1,8-diazacyclotetradeca-4,11-diyne moiety in both molecules is of almost the same structure. The triple bond angles of the six-atom bridges in **2** average to 176.85° , while those in **3** (six-atom bridges



X-ray structure of **2**

only) average to 175.64° due to the increased strain in that molecule. Most of that increased strain however, is on the four-atom bridge as indicated in the most bent of all the triple bonds in the molecule.

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References and Footnotes

- 1 Alder, R.W. *Acc. Chem. Res.* **1983**, 16, 321; *Tetrahedron* **1990**, 46, 683; Alder, R.W. ; East, S. P. *Chem. Rev.* **1996**, 96, 2097 and references therein.

- 2 Gleiter, R.; Hövermann, K.; Ritter, J; Nuber, B. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 789.
- 3 Gleiter, R.; Wolfart, V. *Tetrahedron Lett.* **1996**, *37*, 479.
- 4 Walls, L. P. *Brit. Pat.* 803 072, **1958**; *Chem. Abstr.* **1958**, 53: P 12242i.
- 5 Johnson, A. W. *J. Chem. Soc.* **1946**, 1009.
- 6 **3**: ^1H -NMR (300 MHz in CDCl_3): δ = 2.29 - 2.35(m, 8 H), 2.83-2.91(m, 4 H), 3.11 - 3.20(m, 4 H), 3.42(s, 4 H) - ^{13}C -NMR (75.47 MHz in CDCl_3): δ = 20.7, 43.6, 55.0, 82.0, 85.4 - MS(EI, 70eV): m/z = 240(M^+) - HRMS(EI, 70eV): $\text{C}_{16}\text{H}_{20}\text{N}_2$: calcd. 240.1543, found 240.1585.
- 7 **X-ray structure of 2**: $\text{C}_{18}\text{H}_{24}\text{N}_2$, Mr = 268.41, rhombohedral, space group $R\bar{3}$, crystal size: 0.25 x 0.15 x 0.15 mm, a = 7.493(1) Å, α = 102.02(1)°, V = 388.2(2) Å³, $F_{(000)}$ = 146, Z = 1, $\rho_{\text{calcd.}}$ = 1.148 g cm⁻³, μ = 0.063 mm⁻¹, Mo-K α radiation, λ = 0.71073 Å, Intensity data were collected on a CAD 4 Enraf Nonius diffractometer. Of 519 unique reflections measured, 398 were observed with $I > 3.0\sigma(I)$. The structure was solved by direct methods carried out with SIR⁸, the structure was refined using LSFM MOLEN⁹, R = 0.027, R_w = 0.030.
X-ray structure of 3: $\text{C}_{16}\text{H}_{20}\text{N}_2$, Mr = 240.34, monoclinic, space group $P 2 (1) /c$, crystal size 0.45 X 0.30 X 0.15 mm, a = 7.251(1), b = 21.878(1), c = 8.933(1) Å, α = γ = 90, β = 104.62°, V = 1371.2 Å³, $F_{(000)}$ = 520, Z = 4, $\rho_{\text{calcd.}}$ = 1.164 g cm⁻³, μ = 0.07 mm⁻¹, Intensity data were collected on a SIEMENS-STOE AED2 diffractometer at 200 ° K. Of 3546 reflections collected, 3154 were with $I > 2\sigma(I)$. The structure was solved by direct methods carried out with SHELXS 86 and refined using SHELXL 97¹⁰ with all reflections against F^2 R_1 = 0.046 (only for observed reflections), wR = 0.127.
- 8 Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.* **22**, **1989**, 389-393. Details of the crystal structure determinations of **2** and **3** may be obtained from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB21EW (UK) on quoting the full journal citation.
- 9 Fair, C. K. An Interactive Intelligent System for Crystal Structure Analysis, User Manual, Enraf - Nonius, Delft, The Netherlands. **1990**.
- 10 CRYSTAL STRUCTURE REFINEMENT, UNIX VERSION, Copyright(C) George M. Sheldrick 1993-7 Release 97-1.