Syntheses and Structural Properties of 1,8-Diazacyclotetradeca-3,5,10,12-tetraynes

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The syntheses of 1,8-diazacyclotetradeca-3,5,10,12-tetrayne (**2a**), its *N,N′*-dimethyl (**2b**), *N,N′*-diethyl (**2c**), *N,N′*-diisopropyl (**2d**), *N,N′*-diallyl (**2e**), and *N,N′*-dibenzyl (**2f**) derivatives were achieved in a one-pot procedure from primary amines and 1,6-dibromo-2,4-hexadiyne (**4**). Diffraction studies on single crystals of **2c**–**2f** reveal a chair conformation with the substituents in the diaxial positions. The preference of the axial orientation of the substituents on the nitrogens in **2c**–**2f** is due to several contributions: minimal synaxial 1,3 interactions of the NR bond and the lone pair with adjacent CH and CC bonds.

Introduction

Simple saturated six-membered heterocycles such as piperidine and piperazine adopt the chair conformation with inversion barriers in the order of 10 kcal·mol^{-1}.[1,2] The reason for this preference is that the torsional strain is lower in the chair conformation than in the twist conformation. Substituents at the nitrogen atom(s) of piperidine and piperazine prefer the equatorial orientation. This propensity is due to two main contributions: the 1,3-synaxial and -vicinal interactions between endocyclic methylene groups and substituents as well as between lone pairs are a minimum. To investigate the effects of having no torsional strain between endocyclic methylene groups and no synaxial 1,3-interactions we prepared recently 1,6-diazacyclodeca-3,8-diyne (**1a**) and several of its *N,N′*-disubstituted derivatives.[3]

1

R = H, Me, Et, *i*-Pr, Allyl
a b c d e

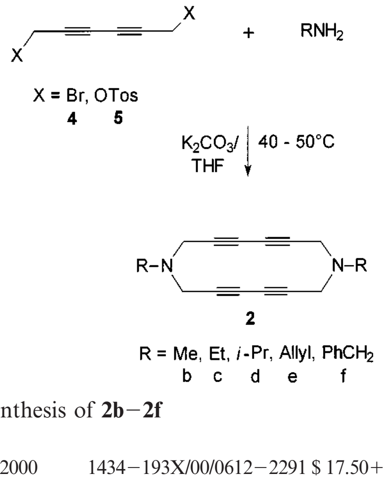
By means of single crystal X-ray diffraction of **1a**−**1e** we found the chair conformation with the bis-axial orientation of the substituents in the solid state.[4] NMR studies in solution reveal a ring inversion barrier ($\Delta G^{\ddagger}$) for **1b** of 11.0 ± 0.3 kcal·mol^{-1} and for **1d** of 10.1 ± 0.3 kcal·mol^{-1}.[4] Trapping of **1d** with concentrated HCl indicates the presence of diequatorial, diaxial, axial and equatorial conformations in solution.[4] The preference of the axial orientation of the substituents on the nitrogen atoms in **1** was attributed to a minimum of vicinal interactions of both the N−R bond and the lone pair with the adjacent C−H and C−C bonds, a minimum of 1,3-synaxial interactions of both the N−R bond and the lone pair, and a minimum of secondary interactions of the C−H and C−C bonds of the alkyl substituent with endocyclic CH$_2$ groups as well as with the triple bonds.[4]

A logical continuation of this research is the extension to cyclic tetraynes. Therefore we have synthesized several *N,N′*-disubstituted 1,8-diazacyclotetradeca-3,5,10,12-tetraynes and studied their structures in the solid state and in solution. In this paper we report on the syntheses and properties of 1,8-diazacyclotetradeca-3,5,10,12-tetrayne (**2a**) and its *N,N′*-dimethyl- (**2b**), *N,N′*-diethyl- (**2c**), *N,N′*-diisopropyl- (**2d**), *N,N′*-diallyl- (**2e**), and *N,N′*-dibenzyl- (**2f**) derivatives.

Results and Discussion

Syntheses

The starting material for our syntheses was 2,4-hexadiyne-1,6-diol (**3**)[5] which was either converted into the dibromide **4**[6] or the bistosylate **5**[7] (Scheme 1). The reac-



Scheme 1. Synthesis of **2b**−**2f**

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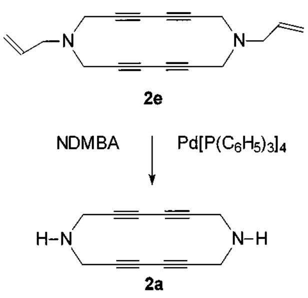
tions of **4** with various primary amines were carried out under high dilution conditions and exclusion of light in the presence of potassium carbonate at 40−50 °C.

To obtain the parent compound **2a** we used the following protocol first proposed by Guibé et al.[8] We treated the temperature-sensitive *N,N′*-diallyl derivative **2e** with *N,N′*-dimethyl barbituric acid (NDMBA) and tetrakis(triphenylphosphane)palladium (Scheme 2) at room temperature.



Scheme 2. Synthesis of **2a**

Structures

Single crystals of the 1,8-diazacyclotetradeca-3,5,10,12-tetrayne derivatives **2c**, **2d**, **2e** and **2f** were obtained by recrystallization from diethyl ether (**2c** and **2f**), THF/*n*-hexane (**2e**) or chloroform (**2d**) at 4 °C. Except for **2e** all the X-ray diffraction experiments were conducted at 200 K to avoid thermal decomposition. The structures of **2d** and **2f** are shown in Figure 1. A crystallographic center of inversion was found in the solid state for **2c**−**2f**.

So far the structures of six congeners have been investigated by means of X-ray diffraction on single crystals: cyclotetradeca-1,3,8,10-tetrayne (**6**),[9] cyclohexadeca-1,3,9,11-tetrayne (**7**),[9] 5,5,6,6,11,11,12,12-octamethylcyclododeca-1,3,7,9-tetrayne (**8**),[10] 5,5,6,6-bis(1,2-cyclohexylene)-11,11,12,12-tetramethylcyclododeca-1,3,7,9-tetrayne (**9**),[11] 2,3,10,11-tetra-*n*-butyldibenzo[*e,k*]cyclododeca-1,3,7,9-tetrayne-5,11-diene (**10**)[12] and 1,2,7,8-tetrakis(triisopropylsilylethynyl)cyclododeca-1,7-diene-3,5,9,11-tetrayne (**11**).[13] In these systems the two 1,3-diyne units are incorporated either in a planar or almost planar 12-membered (**8**−**11**), 16-membered (**7**) or 14-membered (**6**) ring system. In the crystal, the latter two systems adopt the chair conformation (**6**) and the twisted chair-chair conformation (**7**). Common to all of them is a considerable deviation of the two 1,3-diyne units from linearity. The C−C−C angles at the terminal sp centers deviate less from 180° than those at the central sp centers. The 14-membered system of **6** is closest to that of **2**, therefore we have compared the data of **2c**−**2f** with those of **6**[9] in Table 1.

All four structures exhibit a chair conformation with the substituents oriented axially. The most relevant distances are collected in Table 1. In the cases of **2c**−**2f** one observes for the bond lengths of the triple bonds values in the order of 1.19−1.20 Å, and 1.38 Å for the sp−sp single bonds. The angles at the C(sp) centers vary between 172° and 178°.

In all cases the angles at the peripheral C(sp) centers (α, δ) show bigger values than those (β, γ) at the central C(sp) centers. The transannular distances between the peripheral

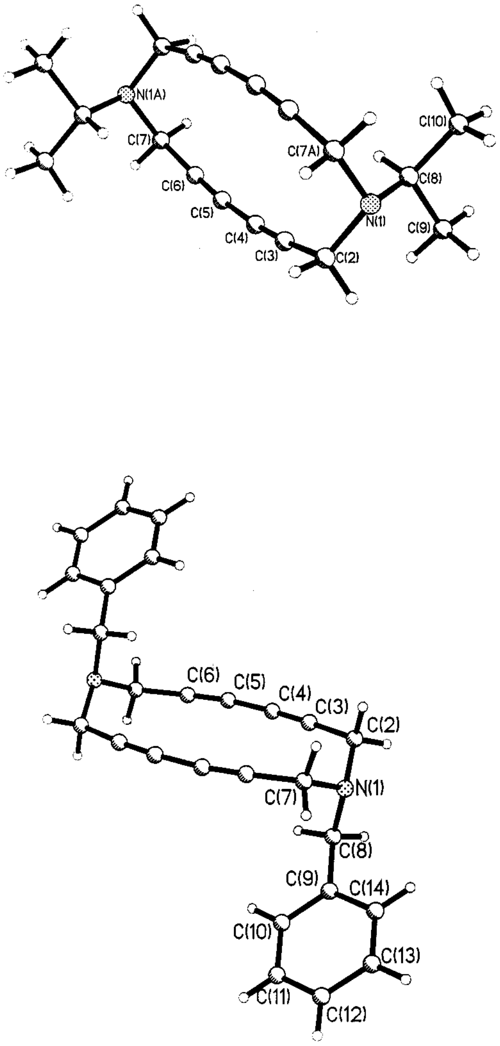


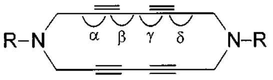
Figure 1. Molecular structures of **2d** and **2f** in the crystal

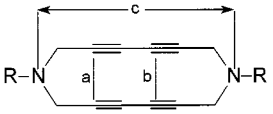
Table 1. Comparison between selected bond lengths (Å) and bond angles (°) of **2c**−**2f** and **6**; for the definition of α, β, γ, δ and **a**, **b**, **c** see text

	2c	2d	2e	2f	6
α	173.6(1)	175.6(1)	174.3(1)	175.7(1)	177.9(1)
β	173.1(1)	172.8(1)	173.3(1)	173.1(1)	172.9(1)
γ	172.5(1)	173.3(1)	172.2(1)	172.6(1)	173.0(2)
δ	176.0(1)	172.1(1)	175.9(1)	174.3(1)	175.6(2)
a	3.074(2)	3.081(2)	3.058(2)	3.067(2)	3.098(2)
b	3.361(2)	3.365(2)	3.351(2)	3.356(2)	3.390(2)
c	7.559(2)	7.505(2)	7.532(2)	7.561(2)	7.593(2)
C(3)−C(4)	1.202(1)	1.197(2)	1.189(4)	1.199(2)	1.194(2)
C(4)−C(5)	1.380(1)	1.382(2)	1.378(4)	1.378(2)	1.385(2)
C(5)−C(6)	1.200(1)	1.198(2)	1.186(4)	1.199(2)	1.195(2)

C(sp) centers (**a**) are shorter (3.06−3.08 Å) than the distances between the inner C(sp) centers (**b**) (3.35−3.37 Å). This difference between the angles and the transannular distances gives the molecule an ellipsoidal shape. In Table 1 we also list the intramolecular distances between the nitrogen atoms (**c**) and compare them with the distances between

C(6) and C(13) of **6**. As anticipated the distances vary only slightly.





Conclusion

Our structural investigations reveal a similarity between the ten-membered rings of *N,N′*-disubstituted 1,6-diazacyclodeca-3,8-diynes and the *N,N′*-disubstituted 1,8-diazacyclotetradeca-3,5,10,12-tetraynes in so far as both adopt the chair-conformation in the solid state and the substituents prefer the diaxial positions. We ascribe the observation that the transannular distances between the peripheral C(sp) centers are smaller than between the inner C(sp) centers to the repulsion between the two 1,3-diyne units.

Experimental Section

Melting points (uncorrected): Dr. Tottoli (Büchi). − ^{1}H NMR (solvent as internal standard): 300 MHz: Bruker AC 300; 500 MHz: Bruker AVANCE 500. − ^{13}C NMR (solvent as internal standard): 75.46 MHz: Bruker AC 300. Unless otherwise noted the ^{1}H NMR spectra were recorded at 300 MHz in CDCl$_3$ and the ^{13}C NMR spectra at 75.46 MHz in CDCl$_3$. − MS: ZAB, Vaccum Generators. − Elemental Analyses: Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

General Procedure for the Synthesis of *N,N′*-Dialkyl-1,8-diazacyclotetradeca-3,5,10,12-tetraynes (2): The reaction was carried out under argon and under the exclusion of light. To a suspension of K$_2$CO$_3$ (40 g) in dry THF were added simultaneously within 8−10 h a solution of 1,6-dibromohexa-2,4-diyne (**4**)[6] (27.8 g, 118 mmol) in THF (500 mL) and the alkylamine (118 mmol) in THF (500 mL) at 40−50 °C. After the addition was complete the mixture was stirred for 2 days. For workup the solution was filtered and concentrated on the rotatory evaporator at 30 °C to 100−200 mL, then adsorbed on 100 g Alox III and chromatographed on silica gel.

***N,N′*-Dimethyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (2b):** The dark brown raw material was adsorbed on 100 g of Alox III. Column chromatography on silica gel (cyclohexane/ether 2:1) yielded 265 mg (2.1%) of **2b** as a light brown solid, m.p. decomp. at room temp. − ^{1}H NMR: δ = 2.55 (s, 6 H), 3.54 (s, 8 H). − ^{13}C NMR: δ = 39.1 (q), 46.7 (t), 71.9 (s), 74.4 (s). − IR (KBr): ṽ = 2968 cm^{-1}, 2932, 2905, 2869, 2797, 2239, 1729. − EI-MS: *m/z* (%) = 210 (6.0) [M$^+$], 209 (20.4) [M$^+$ − 1]. The decomposition of **2b** at room temp. prevented an elemental analysis.

***N,N′*-Diethyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (2c):** The dark brown raw material was adsorbed on 100 g of Alox III. Column chromatography on silica gel (cyclohexane/ethyl acetate 1:1) yielded 390 mg (2.8%) of **2c** as colorless needles, m.p. 110 °C, decomp. − ^{1}H NMR: δ = 1.08 (t, ^3J = 7.2 Hz, 6 H), 2.87 (q, ^3J = 7.2 Hz, 4 H), 3.57 (s, 8 H). − ^{13}C NMR: δ = 12.6 (q), 44.4 (t), 44.7 (t), 71.7 (s), 74.6 (s). − IR (KBr): ṽ = 2969 cm^{-1}, 2906, 2843, 2238, 1632. − $C_{16}H_{18}N_2$ (238.3): calcd. C 80.64, H 7.61, N 11.75; found C 80.52, H 7.58, N 11.77.

***N,N′*-Diisopropyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (2d)**: The dark brown raw material was adsorbed on 100 g of Alox III. Column chromatography on silica gel (cyclohexane/ethyl acetate 1:1) yielded 2.7 g (17.4%) of **2d** as colorless needles, m.p. 100 °C, decomp. − ^{1}H NMR: δ = 1.13 (d, ^3J = 6.3 Hz, 12 H), 3.38 (hept, ^3J = 6.3 Hz, 2 H), 3.62 (s, 8 H). − ^{13}C NMR: δ = 21.2 (q), 43.7 (t), 47.6 (d), 71.9 (s), 76.6 (s). − IR (KBr): ṽ = 2966 cm^{-1}, 2944, 2920, 2868, 2856, 1432. − $C_{18}H_{22}N_2$ (266.2): calcd. C 81.16, H 8.33, N 10.52; found C 80.97, H 8.44, N 10.26.

***N,N′*-Diallyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (2e)**: The dark brown raw material was adsorbed on 100 g of Alox III. Column chromatography on silica gel (cyclohexane/ethyl acetate 10:1) yielded 1.5 g (9.7%) of **2e** as colorless needles, m.p. 110 °C, decomp. − ^{1}H NMR: δ = 3.39 (d, ^3J = 6.6 Hz, 4 H), 3.52 (s, 8 H), 5.39−5.11 (m, ^2J = 1.9 Hz, ^3J = 12.7 Hz, ^3J = 21.7 Hz, ^4J = 1.0 Hz, 4 H), 5.81−5.61 (m, ^3J = 6.6 Hz, 2 H). − ^{13}C NMR: δ = 44.8 (t), 54.1 (t), 72.1 (s), 74.8 (s), 119.0 (t), 134.4 (d). − IR (KBr): ṽ = 3027 cm^{-1}, 3002, 2911, 2889, 2835, 2238, 1879, 1639. − $C_{18}H_{18}N_2$ (262.36): calcd. C 82.39, H 6.92, N 10.68; found C 82.36, H 6.67, N 10.67.

***N,N′*-Dibenzyl-1,8-diazacyclotetradeca-3,5,10,12-tetrayne (2f):** The dark brown raw material was adsorbed on 100 g of Alox III. Column chromatography on silica gel (cyclohexane/ethyl acetate 10:1) yielded 158 mg (0.7%) of **2f** as colorless needles, m.p. 110 °C, decomp. − ^{1}H NMR: δ = 3.58 (s, 8 H), 4.00 (s, 4 H), 7.41−7.26 (m, 10 H). − ^{13}C NMR: δ = 44.6 (t), 55.2 (t), 72.2 (s), 74.7 (s), 127.4 (d), 128.2 (d), 129.1 (d), 137.3 (s). − IR (KBr): ṽ = 3065 cm^{-1}, 3028, 2958, 2912, 2882, 2843, 2817, 2241, 1948, 1870, 1800, 1721, 1631. − $C_{26}H_{22}N_2$ (362.2): calcd. C 86.15, H 6.12, N 7.73; found C 85.97, H 6.17, N 7.69.

Preparation of 1,8-Diazacyclotetradeca-3,5,10,12-tetrayne (2a): The reaction was carried out under argon and light was excluded. To a solution of **2e** (0.5 g, 1.9 mmol) in dry dichloromethane (20 mL) was added a mixture of tetrakis(triphenylphosphane)palladium (0.35 g, 0.3 mmol) and *N,N′*-dimethylbarbituric acid (NDMBA) (3.4 g, 21.6 mmol). The mixture was stirred at room temp. for 2.5 h. For the workup the dark brown solution was extracted with 0.5 N HCl saturated with NaCl. To the aqueous light blue solution was added CHCl$_3$ (50 mL). The pH of the solution was changed to ca. 11 by slow addition of NaCl-saturated 4 N NaOH with ice cooling. Subsequently the aqueous layer was extracted with CHCl$_3$. The organic phases were dried with K$_2$CO$_3$ and the solvent was removed in vacuo. The brown residue was chromatographed on silica gel (CHCl$_3$/methanol 20:1) to yield 96 mg (27.7%) of **2f** as colorless crystals which decompose at 80 °C. − ^{1}H NMR (CF$_3$CO$_2$D): δ = 4.05 (s, 8 H), 11.50 (s, 2 H). − ^{13}C NMR (CF$_3$CO$_2$D): δ = 77.5 (s), 73.6 (s), 42.8 (t). − IR (KBr): ṽ = 3215 cm^{-1}, 2967, 2903, 2238. − HRMS ($C_{12}H_{10}N_2$): calcd. 182.0844; found 182.0831.

X-Ray Structural Analysis of 2c to 2f: The crystallographic data were collected with a Bruker Smart CCD diffractometer (**2c**, **2d**, **2f**) or with a Syntex R3 diffractometer (**2e**). Intensities were corrected for Lorentz and polarization effects. A semiempirical ab-

Table 2. Crystal data and structure refinement for **2c**, **2d**, **2e** and **2f**

Compound	**2c**	**2d**	**2e**	**2f**
Empirical formula	$C_{16}H_8N_2$	$C_{18}H_{22}N_2$	$C_{18}H_{18}N_2$	$C_{26}H_{22}N_2$
Formula weight	238.32	266.38	262.34	362.46
Crystal size [mm]	3 × 0.16 × 0.13	1.85 × 0.44 × 0.09	1.2 × 0.3 × 0.1	0.64 × 0.14 × 0.12
Temperature [K]	200(2)	200(2)	295(2)	200(2)
Wavelength [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	triclinic	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$C2/c$	$P2_1/c$
Z	1	1	4	2
a [Å]	5.1959(6)	5.0749(5)	22.060(10)	5.3774(4)
b [Å]	7.6814(9)	6.6558(7)	5.366(3)	8.8092(7)
c [Å]	9.0326(11)	11.7657(13)	13.870(9)	20.994(2)
α [°]	102.754(2)	96.955(1)	90	90
β [°]	91.957(2)	93.928(1)	112.51(5)	91.259(1)
γ [°]	101.564(2)	95.893(1)	90	90
V [Å^3]	343.31(7)	391.09(7)	1516.8(15)	994.28(13)
$D_{\mathrm{calcd.}}$ [g/cm^3]	1.15	1.13	1.15	1.21
Absorption coefficient, μ [mm^{-1}]	0.07	0.07	0.07	0.07
Theta range for data collection [°]	2.3−25.5	3.10−25.31	2.00−27.50	1.9−25.6
Index ranges	$-6 \leq h \leq 6$ $-9 \leq k \leq 9$ $-10 \leq l \leq 10$	$-6 \leq h \leq 6$ $-7 \leq k \leq 7$ $-13 \leq l \leq 13$	$0 \leq h \leq 28$ $0 \leq k \leq 6$ $-18 \leq l \leq 16$	$-6 \leq h \leq 6$ $-10 \leq k \leq 10$ $-25 \leq l \leq 24$
Reflections collected	2566	2925	1776	7115
Independent reflections	1146 [R(int) = 0.0193]	1296 [R(int) = 0.0225]	1740 [R(int) = 0.0596]	1722 [R(int) = 0.0345]
Observed reflections [$I > 2\sigma(I)$]	961	1081	1131	1346
Max. and min. transmission	0.82 0.54	1.00 0.62	1.00 0.95	0.82 0.45
Data / restraints / parameters	1146/0/118	1296/0/135	1740/0/127	1722/0/171
Goodness-of-Fit on F^2	1.00	1.13	1.13	1.03
R, R_W [$I > 2\sigma(I)$]	0.036, 0.100	0.039, 0.109	0.070, 0.133	0.036, 0.087
$(\Delta\rho)_{\max}$, $(\Delta\rho)_{\min}$ [e Å^{-3}]	0.15, −0.15	0.146, −0.158	0.127, −0.155	0.13, −0.15

sorption correction (multi-scan method) was applied to **2c**, **2d** and **2f** while Ψ-scans were used in the case of **2e**. The structures were solved by direct methods. The non-hydrogen atoms were refined anisotropically according to a full-matrix least-squares technique based on F^2 (**2c**, **2d**, **2f**: SHELXTL-PLUS;[14] **2e**: SHELXL-97[15]). Hydrogen atoms were refined isotropically. The crystallographic data are listed in Table 2.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140020 (**2c**), -140018 (**2d**), -140022 (**2e**), and -140021 (**2f**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

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