Structure of Octamethylene-Bridged Derivatives of 1,3-Cyclohexadiene and Bicyclo[3.1.0]hexene

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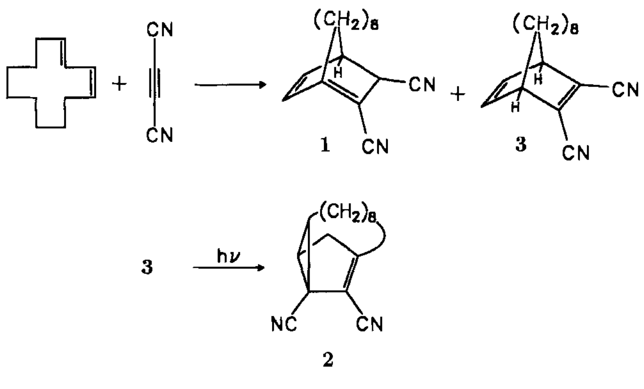
Synthesis and photochemical generation of the octamethylene-bridged 1,3-cyclohexadiene and bicyclo[3.1.0]hexene derivatives **1** and **2**, which are to be classified as anti-Bredt olefins, are reported. *out* Orientation of the octamethylene bridge at the sp^3-hybridized bridgehead atom of **1** generates strain effects while *in* orientation of the bridge in **2** does not give rise to deformations of the bicyclo[3.1.0]hex-2-ene subunit. X-ray analyses indicate a twisted double bond (12.2 and 15.0°) at the bridgehead atom of **1** and a deformation of the six-membered ring from an ideal boat conformation. In contrast, the five-membered ring of compound **2** is planar. The folding angle between the five- and the three-membered ring is 111.8(2)°. The olefinic carbon atoms of **1** are slightly pyramidalized.

In previous studies, we investigated the structure of 1,4-bridged 2,5-cyclohexadienes[1]. Now we report on the synthesis and structure determination of the octamethylene-bridged 1,3-cyclohexadiene derivative 13,14-dicyanobicyclo[8.2.2]tetradeca-1(13),11-diene (**1**) and the photochemical generation and structure determination of the octamethylene-bridged bicyclo[3.1.0]hexene derivative 11,12-dicyanotricyclo[8.2.2.0^{12,13}]tetradec-10-ene (**2**).

Both compounds have double bonds at one bridgehead atom of the oligocyclic system, and, therefore, they are to be classified as anti-Bredt[2] olefins. The octamethylene bridge occupies the *out* position at the saturated bridgehead of compound **1** (Figure 1) and the *in* position at the corresponding atom of compound **2** (Figure 2). Consequently, different strain effects will be expected.



Syntheses

By the reaction of *cis,trans*-1,3-cyclododecadiene with dicyanoacetylene at high pressure (8050 bar, 47°C, 65 h), the Diels-Alder adduct **3** was produced in a yield of 16%[1]. As a minor product we now obtained the bicyclic compound **1** in a yield of 1%. A rearrangement of pure **3** to **1** could not be detected in the following experiments: Treating of pure compound **3** with high temperature (180°C), high pressure (8000 bar), or acidic conditions (HBF_4, HCl). The energetically favoured conjugated 1,3-diene **1** was probably generated in a nonconcerted mechanism in the course of the cycloaddition reaction.

The tricyclic compound **2** was produced by a photochemical rearrangement (−75°C, 700-W mercury high-pressure lamp, 8 h) from the *in,out*-octamethylene-1,4-bridged 2,5-cyclohexadiene **3** in a yield of 41%. This rearrangement is in accordance with the photochemical reaction of corresponding nonbridged 1,4-cyclohexadiene derivatives[3]. An intramolecular photochemical [2 + 2] cycloaddition of the double bonds of **3** could not be observed in contrast to the derivative which has CF_3 groups instead of the cyano substituents[4].

Structure Determination

The molecular structures of compounds **1** and **2** were determined by X-ray structure analyses (Figures 1 and 2).

Since in compound **1** the octamethylene bridge exhibits the *out*-orientation at the sp^3-hybridized bridgehead (C10), the deformation effect of this bridge must be compared with smaller bridges connected to the *in* position. The double bond C1−C13 at the bridgehead atom is twisted [C12−C1−C13−C14 12.2(2)°; C2−C1−C13−C15 15.0(2)°], whereas the second double bond C11−C12 is almost undistorted [C1−C12−C11−C10 1.2(2)°]. The torsional angle along the single bond connecting both double bonds is −34.0(2)° (C11−C12−C1−C13). Because of the twisting and the electron-accepting properties of the cyano substitu-

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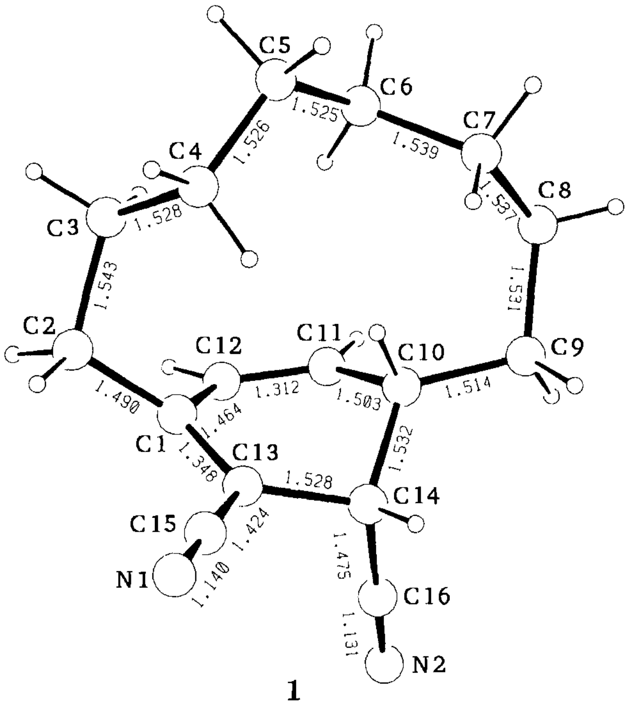
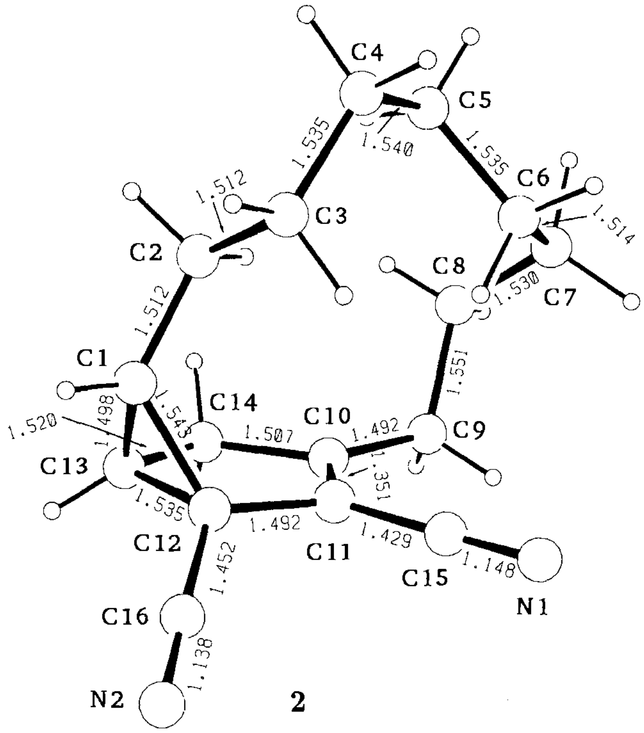


1

Figure 1. Molecular structure with atomic numbering and bond lengths of **1**. The standard deviations are 0.002 Å. ORTEP drawing[8]



2

Figure 2. Molecular structure with atomic numbering and bond lengths of **2**. The standard deviations are 0.002−0.003 Å. ORTEP drawing

ent, the C1−C13 bond [1.348(2) Å] is longer than the undistorted C11−C12 [1.312(2) Å] bond and the bond of ethylene (1.313 Å)[5].

The carbon atoms C11, C12, and C13 are slightly pyramidazlized, by 7 and 3° for C−H and 9.1° for C−CN, into the *exo* direction similar to 1,4-bridged 2,5-cyclohexadienes[1]. Because of 1···4 repulsive interactions [C2···C15 2.953(2) Å], the bond angle C2−C1−C13 [124.2(1)°] is expanded.

The ^{1}H-NMR signal of the hydrogen at the bridgehead, which is oriented inside the large ring system, is observed at rather low field (δ = 3.10) because of many short van der Waals contacts [C7···H10 2.37(1), C8···H10 2.48(1), C1···H10 2.56(1), C6···H10 2.62(1), C4···H10 2.88(1); H7b···H10 2.05(2), H4a···H10 2.16(1), H6a···H10 2.29(2) Å].

The octamethylene bridge attached towards the *in* position at C1 of compound **2** does not give rise to deformations of the bicyclo[3.1.0]hex-2-ene subunit. The five-membered ring (C10 to C14) is planar (±0.03 Å). The torsional angles along the double bond at the bridgehead atom C10 are small [C12−C11−C10−C14 −4.9(2), C9−C10−C11−C15 −1.7(3)°]. The folding angle [111.8(2)°] between the five- and the three-membered ring is in the range of corresponding angles in nonbridged bicyclo[3.1.0]hex-2-ene systems (range from 109.0 to 112.4°)[6].

The bonds of the three-membered ring have unequal lengths because of the electron-accepting influences of the cyano and vinyl substituents[7]. The bond C1−C13, distal to these substituents, is shortened by Δ = −0.027 Å. The shortening effects of cyano and vinyl groups on the distal bonds of cyclopropane derivatives have been determined to be Δ = −0.017 and −0.022 Å[7], respectively. The sum of both values, according to the additivity rule[7], is larger than the shortening effect in **2**. The influence of the vinyl groups is reduced in compound **2** because this substituent deviates by 27.1(2)° from the optimal *cis*-bisected orientation. The double bond C10−C11 [1.351(2) Å] is lengthened by the electron-withdrawing effect of the cyano group (C15−N1).

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Experimental

Melting points (uncorrected): Büchi capillary apparatus. − Microanalyses: Heraeus CHN-rapid device. − IR: Beckman 4240 spectrophotometer. − ^{1}H NMR: Bruker WH 300 spectrometer (300 MHz). − MS: High-resolution ZAB-2F spectrometer (Vacuum Generators).

out-Bicyclo[8.2.2]tetradeca-1(13),11-diene-13,14-dicarbonitrile (**1**): A solution of 1.5 g (9 mmol) of *cis,trans*-1,3-cyclodecadiene in diethyl ether (10 ml) was poured into a solution of 1.0 g (13 mmol) of dicyanoacetylene in diethyl ether (15 ml) at −60°C. After warming up to room temp., the mixture was transferred to a high-pressure autoclave and kept at 47°C and 8050 bar for 65 h. The mixture was then concentrated under reduced pressure, and the remaining dark residue was separated by flash chromatography (silica gel 60, eluent: cyclohexane/ethyl acetate, 2:1). − Crystallization of compound **3** from pentane afforded 340 mg (16%)[1]. Only 20 mg (1%) of colorless **1** were obtained after recrystallization from diethyl ether, m.p. 77−78°C. − ^{1}H NMR (CDCl$_3$, 20°C): δ = 0.8−2.0 (m, 14H, octamethylene bridge, aliphatic), 2.45 and 2.65 (2 × m, 2H, octamethylene bridge, allylic), 2.9 (m, 1H, H−C−CN), 3.1 (m, 1H, bridgehead), 6.4 and 6.45 (2 × m, 2H, olefinic). − MS (70 eV), *m/z* (%): 240 (3) [M$^+$], 211 (6), 197 (6), 183 (6), 156 (18), 144 (15),

Table 1. Crystallograpic data and refinement procedure for **1** and **2**

	1	**2**
Empirical formula	$C_{16}H_{20}N_2$	$C_{16}H_{20}N_2$
Mol. weight [g / mol]	240.4	240.4
Solvent	diethyl ether	pentane / THF
Cryst. size [$\cdot 10^{-1} mm$]	4 · 4.5 · 6.5	2 · 3 · 5
Cryst. color	colorless	colorless
Cryst. system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a [Å]	8.486(2)	7.914(3)
b [Å]	8.927(2)	13.551(2)
c [Å]	10.086(2)	13.120(2)
α [°]	98.55(2)	90
β [°]	92.79(2)	96.73(3)
γ [°]	110.19(2)	90
V [Å^3]	705.0(6)	1397.3(10)
D_{calc} [Mg / m^3]	1.13	1.14
Z	2	4
$F(000)$	260	520
Temperature [K]	293	295
$h_{min} - h_{max}$	0 – 12	–10 – 10
$k_{min} - k_{max}$	–12 – 12	0 – 17
$l_{min} - l_{max}$	–14 – 14	0 – 17
$(sin\Theta/\lambda)_{max}$ [Å^{-1}]	0.66	0.66
μ [m^{-1}]	62.4	63.0
Refl. collected	3623	3494
Refl. independent	3396	3357
Refl. observed	2444	2061
n [I > $n\sigma$(I)]	2.5	3.0
Variables	243	243
$(\Delta/\sigma)_{max}$	0.02	< 0.01
R	0.044	0.044
R_w	0.055	0.057
S (Goodness of fit)	2.33	2.36
$(\Delta\rho)_{max}$ [e · Å^{-3}]	0.15	0.25

142 (15), 129 (27), 116 (22), 81 (23), 67 (28), 55 (81), 41 (100). – IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1} (C–H), 2870, 2210 (CN), 1590, 1480, 1440 (C–H), 1360, 1270, 1240, 900, 770, 745, 680. – $C_{16}H_{20}N_2$ (240.4): calcd. C 79.96, H 8.39, N 11.65; found C 79.93, H 8.24, N 11.60.

Tricyclo[8.2.2.0^{12,13}]tetradec-10-ene-11,12-dicarbonitrile (**2**): 40 mg of bicyclo[8.2.2] tetradeca-11,13-diene-11,12-dicarbonitrile (**3**) (0.2 mmol) were dissolved in 0.4 l of diethyl ether. This solution was irradiated at –75°C for 8 h with a Heraeus TQ718 700-W mercury high-pressure lamp in a Solidex glass photoreactor. After removal of the solvent, the residue was purified by flash chromatography (neutral Al_2O_3, activity I, cyclohexane/ethyl acetate 20:1) to give 18 mg (45%) of tricyclic **2**. Crystallization from pentane/THF at –20°C yielded prisms, m.p. 144°C. – ^{1}H NMR ($CDCl_3$, 21°C): δ = 0.67–1.87 (m, 16H, CH_2 and CH), 2.34–2.82 (m, 4H, allylic). – MS (70 eV), *m/z* (%): 240 (17) [M$^+$], 211 (32), 197 (28), 142 (77), 129 (36), 69 (50), 55 (68), 41 (100). – IR (KBr): $\tilde{\nu}$ = 2935 cm^{-1} (C–H), 2220, 2210 (CN), 1620, 1445 (C–H), 745. – $C_{16}H_{20}N_2$ (240.4): calcd. C 79.96, H 8.39, N 11.65; found C 80.14, H 8.38, N 11.62.

Collection of X-Ray Data and Structure Solution: The X-ray data (Table 1) were collected on an automated diffractometer (Enraf-Nonius CAD4, graphite monochromator, Mo-K_α radiation, ω – 2Θ scan). The structures were solved by direct methods (Multan[9]). The structural parameters (C and N anisotropic, H isotropic) were refined by full-matrix least-squares technique. All calculations were performed with the SDP program package[10]. Further details of the structure investigation are avilable on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the despository numbers CSD-400483 (**1**) and CSD-400482 (**2**), the names of the authors, and the journal citation.

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