Pyramidalization of the sp²-Hybridized Carbon Atoms in 1,4-Bridged 2,5-Cyclohexadienes

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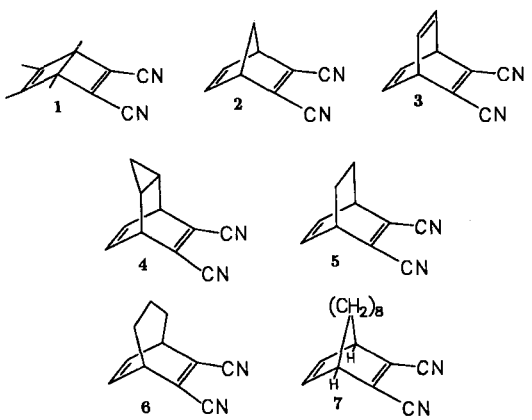
The 2,5-cyclohexadiene-2,3-dicarbonitrile derivatives **1**–**7**, the 1,4-positions of which are linked by bridges with increasing lengths, have been prepared in order to determine the influence of the bridging on the structural parameters of this system. Therefore, we have examined the molecular structures of **1**–**7** by X-ray analyses. Depending on the length of the bridge, the *endo* pyramidalization of the sp²-hybridized carbon atoms established for **1** and **2** changes into *exo* orientation in the derivatives **5**–**7** to prevent eclipsed conformations between the substituents on the double bonds and on the bridgehead atoms. The intramolecular distances and folding angles of **2**–**7** vary systematically with the length of the bridges except the distance between the double bonds which is fixed to a magnitude of 2.42–2.45 Å. The syntheses of the compounds **1**, **4**, and **7** have not yet been reported in the literature.

Several experimental and theoretical investigations deal with the pyramidalized sp²-hybridized carbon atoms of norbornene and norbornadiene systems[1]. As a consequence of the structural distortion the density distributions of the π electrons are asymmetrically deformed as shown theoretically[1c,d,j] and established experimentally[1m]. Moreover, the *exo* and *endo* reactivity of these π systems differ considerably[1a–f]. Repulsive interactions and hyperconjugative effects have been discussed as the reasons for these deformations[1a–j]. For all these compounds an *endo* deviation of the substituents on the sp²-hybridized carbon atoms have been recorded (*anti* to the methylene or bismethylene bridge)[1].

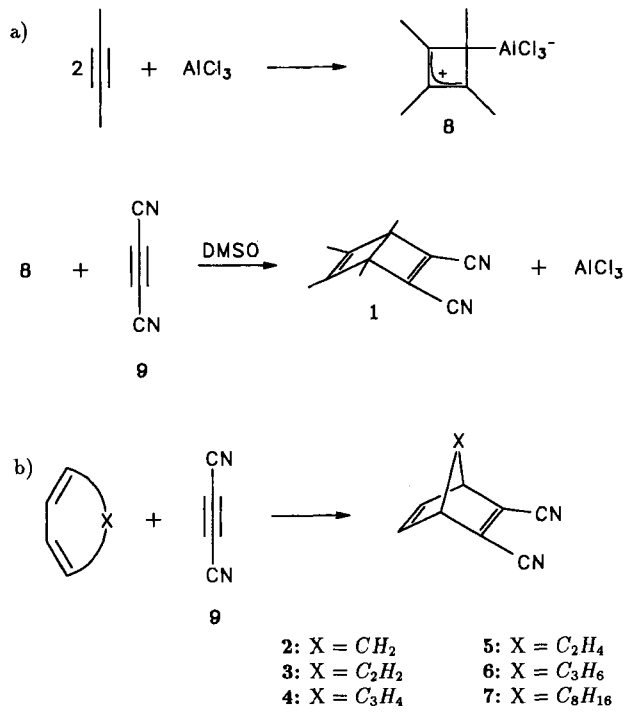
We have investigated systematically the bridged 2,5-cyclohexadienes **1**–**7** by X-ray structure analyses in order to determine the kind and the degree of molecular deformations and their correlation with the length of the bridge. The cyano substituents enable us to decide the deviations precisely. On the other hand, we can compare them with the corresponding deviations of the hydrogen atoms on the opposite side.



Syntheses

Dewar benzene derivative **1** is obtained by the reaction of two equivalents of 2-butyne with one equivalent of $AlCl_3$ in dichloromethane[2]. The resulting red aluminum σ complex **8** reacts with butynedinitrile[3] (**9**) in DMSO to form **1** (Scheme 1a). All other compounds (**2**–**7**) have been prepared by Diels-Alder synthesis (Scheme 1b). They are obtained by the reaction of cyclic 1,3-dienes (or benzene in the

Scheme 1



2: X = CH_2 **5**: X = C_2H_4
3: X = C_2H_2 **6**: X = C_3H_6
4: X = C_3H_4 **7**: X = C_8H_{16}

  0009–2940/92/0909–2067 $ 3.50+.25/0

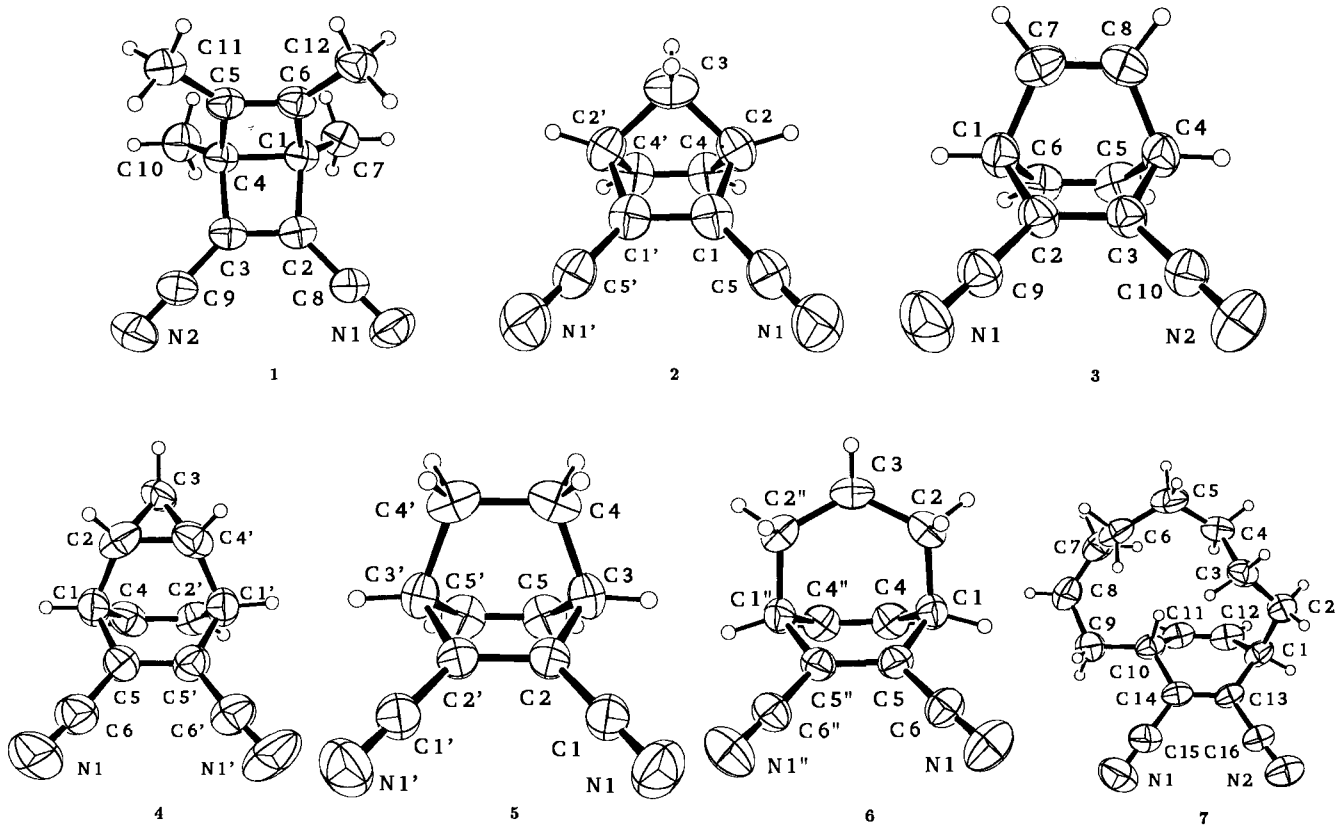


Figure 1. Molecular structures with atomic numbering of **1**–**7**. Only one of both independent molecules of compound **2** is shown

case of **3**) with **9** (Scheme 1b). Thus compound **2**[3] is synthesized by treatment of cyclopentadiene with **9** and compound **3**[4] by treatment of benzene with **9** in the presence of $AlCl_3$ as catalyst. By heating 1,3,5-cycloheptatriene, which will be partly converted to norcaradiene, with **9** we obtain **4**. In a similar manner, 1,3-cyclohexadiene reacts with **9** to furnish bicyclo[2.2.2]octadienedicarbonitril **5** by warming up the reaction mixture from −195 to 20°C[5]. Compound **6** is synthesized[6] from **9** and 1,3-cycloheptadiene, which has been obtained by Birch reduction of 1,3,5-cycloheptatriene[7]. Allylic bromination of cyclododecene followed by elimination of HBr from 3-bromo-1-cyclododecene on basic Al_2O_3 gives 1,3-cyclododecadiene[8] which is purified by flash chromatography[9]. Because cyclododecadiene is sterically unfavorable to be subjected to the Diels-Alder reaction, compound **7** has been prepared in sufficient amounts by cycloaddition reaction of this dodecadiene with **9** only at a pressure of 8000 atm and 45°C for 48 h. The compounds **1**, **4** and **7** have not yet been reported in the literature.

Molecular Structures and Structural Comparison of 1–7

The molecular structures of **1**–**7** were determined by X-ray structure analyses (Figure 1). In the crystals of **2** (*Pnma*; $Z = 8$; two independent molecules), **5** (*Pnma*; $Z = 4$) and in **6** (*Pnma*; $Z = 4$) all the independent molecules lie on a crystallographic mirror plane, and **4** ($P4_12_12$; $Z = 4$) is disordered around a twofold rotation axis. The $(CH_2)_8$ bridge of **7** is connected to the *in* position on one side and to the *out* position on the other side (Figure 1). For comparison with the derivatives **1**–**6** we can use only the parameters on the *in* side of **7**. In Table 1 several molecular parameters are given.

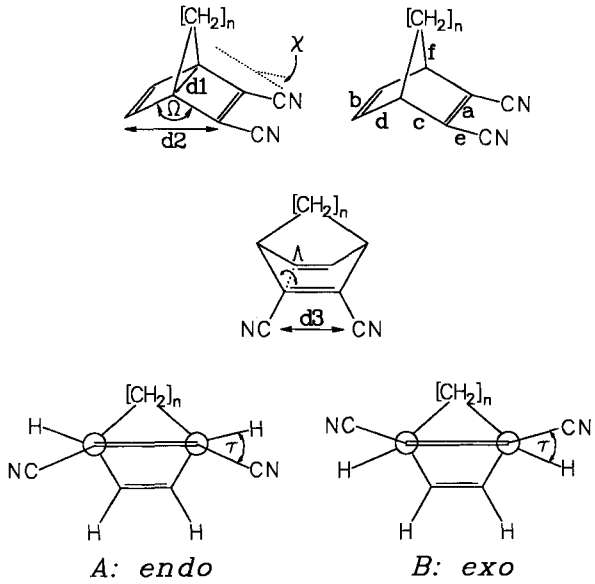


Figure 2. Symbols for Table 1–3

The substituents of the Dewar benzene **1** deviate by $\chi = 1.3(2)°$ (CN) and $1.9(2)°$ (CH_3) from the double bond plane into *endo* direction (away from the bridge) (Table 1) as pre-

Table 1. Molecular parameters of **1**–**7**. Symbols are defined in Figure 2. Parameter d2 is the averaged value of the nonbonding distances between all opposite atomic positions of the double bonds for each molecule. Λ, τ, χ_C and χ_H represent folding, torsional, and bending angles, which are averaged, if possible. τ_C means the H–C–C–CN torsional angle, τ_H represents the H–C–C–H angle. χ designates the out-of-plane deviation of substituents on the double bond from the *endo/exo* direction. It is defined as the angle between the plane consisting of a bridgehead and both double bond atoms and the plane of the same two double bond atoms and the substituent atom. For **1** the hydrogen atoms at the double bond are replaced by methyl groups. The parameters of **2** are averaged between two independent molecules

Compound	1	2	3	4	5	6	7	
d1 [Å]	1.575(3)	2.223(2)	2.535(2)	2.554(4)	2.558(2)	2.750(2)	2.845(4)	
d2 [Å]	2.569(2)	2.449(2)	2.430(2)	2.416(4)	2.444(2)	2.446(2)	2.450(4)	
d3 [Å]	3.254(3)	3.061(2)	2.987(2)	2.925(5)	2.921(2)	2.891(2)	2.842(4)	
Ω [°]	114.9(2)	113.9(1)	119.3(2)	118.7(3)	123.8(2)	132.8(2)	138.5(3)	
Λ [°]	98.4(2)	119.4(1)	130.4(2)	129.4(3)	133.1(2)	143.0(2)	153.9(3) (143.3(3))	
τ_H [°]	55.3(3)	19.2(12)	1.9(13)	—	6.7(10)	19.7(12)	37.4(21)	
τ_C [°]	55.3(3)	18.4(9)	0.5(9)	4.2(20)	3.4(8)	17.8(8)	32.3(15)	
χ_C [°]	1.3(2)	1.5(1)	0.7(1)	—			0.7(2)	endo
				—	1.2(1)	2.3(1)		exo
χ_H [°]	1.9(2)	2.9(11)	1.1(12)	—				endo
				—	3.3(11)	2.3(9)	5.9(17)	exo

dicted for Dewar benzene derivatives by theoretical calculations[1i,n,10] and determined by X-ray structure analyses[11].

In the same way as **1** compound **2** shows small *endo* pyramidalization of its substituents by 1.5(1) (χ_C) and 2.9(11)° (χ_H), averaged between both independent molecules. This is in accordance with theoretical calculations[1d,h,i,n,12], which predict *endo* pyramidalizations in the magnitude of 1.7 to 6.4°. The same effect was detected by NMR investigations in nematic phases (4.0°)[13] and X-ray structure determinations (range from 1.9 to 8.6°)[1k,14,15,16]. 1,4-Cyclohexadiene, not substituted and not bridged, which can be regarded as norbornadiene without bridge, is completely planar[17].

In contrast to **1** and **2**, the substituents on the double bonds of **5** deviate by χ_C 1.2(1) and χ_H 3.3(11)° to the *exo* direction (Table 1). Comparable *exo* deviations are found for all other bicyclo[2.2.2]octa-2,5-dienes if the corresponding molecular parameters are calculated with the reported atomic coordinates [0.9–6.8° (χ_C), 3.4–6.5° (χ_H)][18–22]. Only derivatives which are not substituted on the bridgehead atoms and which are not deformed by intramolecular strain effects, were selected from the Cambridge Structural Database[23]. Tricarbonyl[η^4-(bicyclo[2.2.2]octa-2,5-diene-2,3-dicarbonitrile)]-iron(0)[24] (**10**), the $Fe(CO)_3$ complex of **5**, shows much larger deformations to the *exo* side with the values of 24.4(2) (χ_C) and 7.6(16)° (χ_C), , of which the greatest part is generated by complexation.

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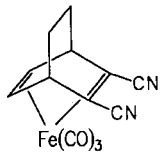

If we increase the length of the methylene bridge even more (n = 3: **6**), the substituents on the double bonds are bent in the *exo* direction too [χ_C = 2.3(1), χ_H = 2.3(9)°]. The deviation χ_C on the comparable *in* side of compound **7** with the *out-in* $(CH_2)_8$ bridge is not significant (Table 1) because the unsymmetrical bridging generates additional deformations. The double bond is significantly twisted [C1–C13–C14–C10 –7.3(4), C15–C14–C13–C16 –7.3(4)°].

Compound **3** cannot display a preferred bending orientation of the cyano groups because of its high molecular symmetry C_{2v} (Table 1): small χ_C and χ_H values indicate the position near the turning point of pyramidalization. Compound **4** exhibits disorder effects between the cyclopropane ring and the unsubstituted double bond. Therefore, compound **4** cannot be discussed in this respect.

The χ_C deviations of **1**, **2**, and **5**–**7** are small but significant. The corresponding deviations χ_H of the hydrogen atoms have the same direction as in the case of the cyano groups, but they are not always significant. There is a border between **2** (n = 1) and **5** (n = 2) where the χ deviation switches from *endo* to *exo* direction (Figure 2: **A** and **B**), depending on the length of the $(CH_2)_n$ bridge which determines particulary the direction of the C–H bond at the bridgehead atom.

The substituents on the double bonds and on the bridgehead atoms try to prevent an eclipsed conformation as far as possible. Thus repulsive interactions between the substituents and closed-shell repulsions result in an *endo* deviation of the substituents at the double bond for n = 0, 1 (**A**, Figure 2) and an *exo* bending for $n \geq 2$ (**B**, Figure 2). This effect could be confirmed by combined force-field and quantum-mechanical calculations (Table 2)[25].

According to these calculations the energy values (Table 2) indicate a decrease of strain from **1** to **6**. The higher strain energy of **7** is obviously caused by additional angular and torsional strain of the octamethylene bridge and the repulsion between these groups and H 10 in the *in* position of the bridgehead carbon atom C 10.

Table 2. Deviations obtained by force-field/MNDO calculations[25] for the compounds **1**–**7**. For **1** the hydrogen atoms are replaced by methyl groups

Compound	1	2	5	6	7	
χ_{CN} [°]	0.9	2.1				endo
			0.6	2.5	1.7	exo
χ_H [°]	0.6	1.2				endo
			0.6	1.9	0.8	exo
Strain energy [kcal]	64	29	19	17	35	

Selected bond lengths are given in Table 3. As shown in Table 1 the intramolecular nonbonding distances (d1, d3) and interplanar angles (Λ, Ω) change gradually with variing *n*. A comparison of the Dewar benzene **1** with the bridged cyclohexadienes **2**–**7** is restricted, because chemically these systems differ in many respects. With increasing *n* the molecular parameters d1, Ω, and Λ increase (Table 1) which marks a flattening of the cyclohexadiene ring, and therefore d3 decreases (Table 1). The distance d2 does not show any dependence on *n* and has the same order of magnitude for all $n = 1-8$ (Table 1). Obviously, the repulsion between both π systems plays a dominant part, which cannot be affected by sterical changes of the surroundings.

Table 3. Bond lengths [Å] in **1**–**7** (Figure 2). The values in brackets for **7** refer to *out* bridge

Bonds	1	2	3	4	5	6	7
a	1.336(3)	1.339(2)	1.334(2)	1.349(4)	1.346(1)	1.342(2)	1.336(4)
b	1.328(3)	1.315(2)	1.311(2)	—	1.325(2)	1.319(2)	1.320(4)
c	1.531(2)	1.529(2)	1.536(2)	1.518(4)	1.517(2)	1.515(2)	1.523(3) (1.510(4))
d	1.529(2)	1.527(2)	1.531(2)	—	1.512(2)	1.508(2)	1.509(4) (1.519(4))
e	1.423(3)	1.422(2)	1.431(2)	1.415(5)	1.428(2)	1.435(2)	1.429(4) (1.446(4))
f	1.575(3)	1.539(2)	—	—	1.559(2)	1.552(2)	1.554(4) (1.522(4))

Table 4. Crystallographic data and refinement procedure for **1**–**7**

	1	2	3	4	5	6	7
Empirical formula	$C_{12}H_{12}N_2$	$C_9H_6N_2$	$C_{10}H_6N_2$	$C_{11}H_8N_2$	$C_{10}H_8N_2$	$C_{11}H_{10}N_2$	$C_{16}H_{20}N_2$
Mol. weight [g / mol]	184.2	142.2	154.2	168.2	156.2	170.2	240.4
Solvent	n-pentane	ethanol / THF	ethanol	ethanol	methanol	isopropanol	n-pentane
Cryst. size [$\cdot 10^{-1}mm$]	4 · 3 · 3	6 · 4 · 2	5 · 5 · 4	5 · 5 · 4	5 · 4 · 4	5 · 3.5 · 3	5 · 5 · 5
Cryst. color	colorless	colorless	colorless	colorless	colorless	colorless	colorless
Cryst. system	triclinic	orthorhombic	orthorhombic	tetragonal	orthorhombic	orthorhombic	monoclinic
Space group	$P\bar{1}$	*Pnma*	*Pbca*	$P4_12_12$	*Pnma*	*Pnma*	$P2_1/n$
a [Å]	7.201(2)	10.981(2)	12.439(2)	8.486(2)	11.762(2)	6.818(1)	9.147(3)
b [Å]	8.976(2)	11.570(1)	8.300(1)	8.484(2)	11.531(2)	12.103(2)	14.219(3)
c [Å]	9.137(2)	11.804(2)	15.368(3)	12.525(3)	6.069(1)	11.218(2)	10.604(3)
α [°]	98.77(2)	90	90	90	90	90	90
β [°]	100.72(2)	90	90	90	90	90	91.71(2)
γ [°]	105.93(2)	90	90	90	90	90	90
V [Å^3]	544.9(6)	1499.7(7)	1586.6(8)	901.8(5)	823.5(4)	925.7(5)	1378.6(11)
D_{calc} [Mg / m^3]	1.12	1.26	1.29	1.24	1.26	1.22	1.16
Z	2	8	8	4	4	4	4
F(000)	196	592	640	352	328	360	520
Temperature [K]	230	295	295	295	295	295	295
$h_{min} - h_{max}$	0 – 9	0 – 14	0 – 16	0 – 11	0 – 15	0 – 9	-12 – 12
$k_{min} - k_{max}$	-11 – 11	0 – 15	0 – 10	0 – 11	0 – 15	0 – 14	0 – 18
$l_{min} - l_{max}$	-12 – 12	0 – 15	0 – 20	0 – 16	0 – 8	0 – 15	0 – 14
$(sin\Theta/\lambda)_{max}$ [Å^{-3}]	0.66	0.66	0.66	0.66	0.66	0.66	0.66
μ [m^{-1}]	63.2	72.8	74.2	70.6	72.1	69.3	63.8
Refl. collected	2822	1898	1898	693	1038	1150	3481
Refl. independent	2615	1898	1898	682	1036	1150	3311
Refl. observed	1702	1155	1286	506	785	810	1737
n [I > $n\sigma$(I)]	2.5	3.0	2.5	2.5	3.0	2.5	2.5
Variables	175	131	133	77	71	96	259
$(\Delta/\sigma)_{max}$	<0.01	<0.01	<0.01	<0.01	<0.01	0.01	<0.01
R	0.054	0.038	0.037	0.053	0.038	0.043	0.067
R_w	0.063	0.046	0.046	0.077	0.054	0.051	0.075
S (Goodness of fit)	2.55	1.99	1.96	3.49	2.49	2.24	3.09
$(\Delta\rho)_{max}$ [e · Å^{-3}]	0.34	0.11	0.13	0.16	0.14	0.14	0.24

Table 5. Atomic coordinates and the equivalent atomic displacement parameters ($\cdot 10^3$ Å^2) of **1**–**7**. $U_{eq} = 1/3 \sum \sum U_{ij} a_i^* a_j^* \boldsymbol{a}_i \cdot \boldsymbol{a}_j$

1 Atom	x	y	z	U_{eq}
N1	0.3142(3)	0.6299(2)	-0.2289(2)	75(1)
N2	0.1354(3)	0.2701(2)	0.1016(2)	71(1)
C1	0.4096(2)	0.8207(2)	0.1857(2)	43(1)
C2	0.3341(2)	0.6716(2)	0.0577(2)	44(1)
C3	0.2839(2)	0.5723(2)	0.1491(2)	44(1)
C4	0.3503(2)	0.7038(2)	0.2936(2)	44(1)
C5	0.5723(2)	0.7552(2)	0.3685(2)	45(1)
C6	0.6227(2)	0.8534(2)	0.2774(2)	45(1)
C7	0.3283(3)	0.9562(2)	0.1679(2)	55(1)
C8	0.3236(3)	0.6462(2)	-0.1018(2)	51(1)
C9	0.2032(3)	0.4045(2)	0.1213(2)	50(1)
C10	0.2014(3)	0.7148(2)	0.3879(2)	60(1)
C11	0.6798(3)	0.7014(2)	0.4940(2)	56(1)
C12	0.8111(3)	0.9595(2)	0.2584(2)	57(1)

2 Atom	x	y	z	U_{eq}
N1	0.4321(1)	0.0559(1)	-0.1399(1)	72(1)
N11	0.3876(1)	0.5569(1)	0.4048(1)	89(1)
C1	0.3852(1)	0.3080(1)	0.0262(1)	46(1)
C2	0.3510(1)	0.3463(1)	0.1461(1)	51(1)
C3	0.4177(2)	0.2500	0.2110(2)	62(1)
C4	0.2197(1)	0.3070(1)	0.1656(1)	50(1)
C5	0.4108(1)	0.3824(1)	-0.0666(1)	52(1)
C11	0.5721(1)	0.8077(1)	0.3957(1)	46(1)
C22	0.7053(1)	0.8459(1)	0.3953(1)	51(1)
C33	0.7567(2)	0.7500	0.3184(2)	56(1)
C44	0.7593(1)	0.8067(1)	0.5080(1)	56(1)
C55	0.4690(1)	0.8821(1)	0.4004(1)	57(1)

3 Atom	x	y	z	U_{eq}
N1	0.5850(1)	0.7864(1)	0.0982(1)	70(1)
N2	0.7219(1)	0.4324(2)	-0.0786(1)	68(1)
C1	0.5285(1)	0.4043(2)	0.1990(1)	45(1)
C2	0.5812(1)	0.4787(1)	0.1184(1)	41(1)
C3	0.6247(1)	0.3699(2)	0.0651(1)	40(1)
C4	0.6108(1)	0.1961(2)	0.0984(1)	46(1)
C5	0.6593(1)	0.1960(2)	0.1900(1)	52(1)
C6	0.6172(1)	0.3049(2)	0.2418(1)	51(1)
C7	0.4470(1)	0.2833(2)	0.1625(1)	49(1)
C8	0.4894(1)	0.1760(2)	0.1106(1)	49(1)
C9	0.5836(1)	0.6500(2)	0.1055(1)	47(1)
C10	0.6788(1)	0.4055(2)	-0.0145(1)	45(1)

4 Atom	x	y	z	U_{eq}
N1	1.0228(5)	-0.2563(4)	0.3823(3)	108(2)
C1	0.7816(4)	0.0809(4)	0.3279(2)	58(2)
C2	0.8339(4)	0.2468(4)	0.3570(2)	62(2)
C3	0.7584(7)	0.3855(6)	0.3083(5)	56(3)
C4	0.6773(4)	0.0895(3)	0.2284(3)	61(2)
C5	0.9299(3)	-0.0030(4)	0.2909(2)	53(1)
C6	0.9858(4)	-0.1429(4)	0.3393(2)	67(2)

5 Atom	x	y	z	U_{eq}
N1	0.7245(1)	0.0680(1)	-0.1341(2)	63(1)
C1	0.7898(1)	0.1234(1)	-0.0428(2)	43(1)
C2	0.8734(1)	0.1917(1)	0.0679(2)	38(1)
C3	0.9696(1)	0.1391(1)	0.2010(2)	43(1)
C4	0.9513(1)	0.1839(1)	0.4408(2)	53(1)
C5	1.0794(1)	0.1926(1)	0.1205(2)	49(1)

6 Atom	x	y	z	U_{eq}
N1	0.3457(2)	0.0768(1)	0.3164(1)	66(1)
C1	0.2505(2)	0.1364(1)	0.0107(1)	43(1)
C2	0.4451(2)	0.1420(1)	-0.0608(1)	56(1)
C3	0.4850(5)	0.2500	-0.1237(2)	52(1)
C3'	0.5377(11)	0.2500	-0.0695(6)	60(4)
C4	0.0883(2)	0.1955(1)	-0.0547(1)	50(1)
C5	0.2819(2)	0.1945(1)	0.1288(1)	38(1)
C6	0.3172(2)	0.1306(1)	0.2343(1)	44(1)

7 Atom	x	y	z	U_{eq}
N1	0.2655(3)	0.0810(2)	0.3037(2)	90(2)
N2	0.6964(3)	0.0908(2)	0.4233(2)	75(2)
C1	0.5336(3)	0.2089(2)	0.6761(2)	53(1)
C2	0.5739(3)	0.1413(2)	0.7869(3)	59(2)
C3	0.4562(4)	0.0709(2)	0.8306(3)	55(2)
C3'	0.4634(16)	0.1284(12)	0.8929(14)	44(8)
C4	0.3480(4)	0.1128(2)	0.9228(3)	59(2)
C4'	0.3695(17)	0.0374(13)	0.8654(14)	45(8)
C5	0.2142(4)	0.0502(2)	0.9441(3)	68(2)
C6	0.0959(4)	0.0524(2)	0.8387(3)	64(2)
C6'	0.1096(18)	0.1055(11)	0.8941(16)	48(9)
C7	0.0260(4)	0.1477(3)	0.8127(3)	70(2)
C7'	0.0259(24)	0.0730(15)	0.7670(18)	80(12)
C8	-0.0314(3)	0.1670(3)	0.6809(3)	81(2)
C9	0.0741(3)	0.1623(2)	0.5721(3)	70(2)
C10	0.2334(3)	0.1756(2)	0.6136(2)	50(1)
C11	0.2798(3)	0.2701(2)	0.6683(2)	57(1)
C12	0.4189(3)	0.2823(2)	0.7010(2)	60(2)
C13	0.4891(3)	0.1568(2)	0.5555(2)	45(1)
C14	0.3481(3)	0.1459(2)	0.5222(2)	47(1)
C15	0.3031(3)	0.1072(2)	0.4011(3)	60(2)
C16	0.6026(3)	0.1210(2)	0.4792(2)	54(1)

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Experimental

Melting points: Büchi capillary apparatus (Dr. Tottoli), uncorrected. – Microanalyses: Heraeus CHN Rapid device. – IR: Beckman 4240 and Bruker IFS 85 FT-IR spectrophotometer. – ^{1}H NMR: 300 MHz, Bruker WH 300 spectrometer. – MS: High-resolution ZAB-2F spectrometer (Vacuum Generators).

1,4,5,6-Tetramethylbicyclo[2.2.0]hexa-2,5-diene-2,3-dicarbonitrile (**1**): To 3.1 g (13 mmol) of the red complex **8**[2] freshly prepared butynedinitrile[3] (**9**, 1.0 g, 13 mmol), dissolved in dichloromethane (20 ml), was added with stirring at −50°C. After warming to 0°C, the solution was stirred at this temp. for 5 h, then an excess of DMSO (100 ml) in dichloromethane (40 ml) was added. This mixture was poured into ice/water, then extracted with dichloromethane. The extract was washed with water, dried with Na_2SO_4, and the solvent was evaporated to yield crude **1**. Flash chromatography[9] on silica gel with toluene and crystallization from pentane at −10°C afforded 0.1 g (4%) of **1** as colorless crystals, m.p. 75°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 1.34 (s, 2 CH_3), 1.66 (s, 2 CH_3). – MS (70 eV): *m/z* (%) = 184 (75) [M^+], 169 (100) [$M^+ - CH_3$]. – IR (KBr): $\tilde{\nu}$ = 2205 cm^{-1}, 2200 (CN), 1600 (C=C).

$C_{12}H_{12}N_2$ (184.2) Calcd. C 78.23 H 6.57 N 15.21
Found C 78.09 H 6.64 N 15.20

Tricyclo[3.2.2.0^{2,4}]nona-6,8-diene-6,7-dicarbonitrile (**4**): 1,3,5-cycloheptatriene (1.8 g, 20 mmol) was added dropwise at −60°C to a solution of **9** (1.0 g, 13 mmol) in dichloromethane (10 ml). The mixture was allowed to warm up to room temp. After 1.5 h the reaction mixture was refluxed with stirring for 5 h. Removal of the solvent followed by flash chromatography of the residue with silica gel 60 (eluent: cyclohexane/ethyl acetate, 2:1) and crystallization from ethanol afforded 0.5 g (24%) of **4** as colorless prisms, m.p. 136°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 6.08 (s, 2H olefinic), 4.08 (s, 2H, allylic), 1.50 (s, 2H methylene), 0.88 (m, 1H), 0.75 (m, 1H). – MS (70 eV): *m/z* (%) = 168 (100) [M^+], 167 (78) [$M^+ - H$], 142 (25) [$M^+ - C_2H_2$], 141 (95) [$M^+ - H - C_2H_2$], 140 (96) [$M^+ - C_2H_4$], 114 (33) [$M^+ - CN - C_2H_4$], 39 (35) [C_3H_3]. – IR (KBr): $\tilde{\nu}$ = 3010 cm^{-1} (C–H), 2215 (CN), 1339, 1248, 1045, 838, 820, 747, 688 (C=C, out-of-plane).

$C_{11}H_8N_2$ (168.2) Calcd. C 78.55 H 4.79 N 16.66
Found C 78.53 H 4.76 N 16.64

out,in-Bicyclo[8.2.2]tetradeca-11,13-diene-11,12-dicarbonitrile (**7**): A cooled mixture (−60°C) of 1.0 g (13 mmol) of butynedinitrile (**9**), dissolved in diethyl ether (15 ml), and 1.5 g (9 mmol) of *cis,trans*-1,3-cyclododecadiene, dissolved in diethyl ether (10 ml), was allowed to warm up to room temp. Afterwards, it was transferred to a high-pressure autoclave and kept 48 h at 47°C and 8050 bar. The solvent was removed and the remaining dark mixture separated by flash chromatography with silica gel 60 (eluent: cyclohexane/ethyl acetate, 2:1). Crystallization from pentane afforded 0.34 g (16%) of colorless **7**, m.p. 74°C. – ^{1}H NMR ($CDCl_3$, 20°C): δ = 0.83–2.26 (m, 16H, octano bridge), 3.12 (m, 1H, *in*), 3.41 (m, 1H, *out*), 5.92 (m, 2H, olefinic). – MS (70 eV): *m/z* (%) = 240 (12) [M^+], 239 (33) [$M^+ - H$], 211 (31) [$M^+ - H - C_2H_4$], 156 (37) [$M^+ - C_6H_{12}$], 155 (24) [$M^+ - H - C_6H_{12}$], 142 (73) [$M^+ - C_7H_{14}$], 129 (64) [$M^+ - C_8H_{15}$], 69 (28) [C_5H_9], 55 (79) [C_4H_7], 41 (100) [C_3H_5]. – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} (C–H), 2840, 2210 (CN), 1585, 1480, 1440 (C–H), 900, 770, 745, 680.

$C_{16}H_{20}N_2$ (240.4) Calcd. C 79.95 H 8.39 N 11.66
Found C 79.75 H 8.37 N 11.61

Collection of X-ray Data and Structure Solution: The X-ray data (Table 4) 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[26]). The structural parameters (C and N anisotropic, H isotropic) were refined by full-matrix technique. Disorder effects occurred between the three-membered ring and the unsubstituted double bond in compound **4**, on the central carbon atom of the propano bridge in **6** (two positions) and in four bridging methylene groups of 7 (these four atoms have additional positions which are marked with an apostrophe and refined only isotropically). The atomic coordinates are given in Table 5. Further details of the structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-7514 Eggenstein-Leopoldshafen 2, on quoting the depository number CSD-56210, the names of the authors, and the journal citation.

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