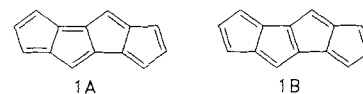
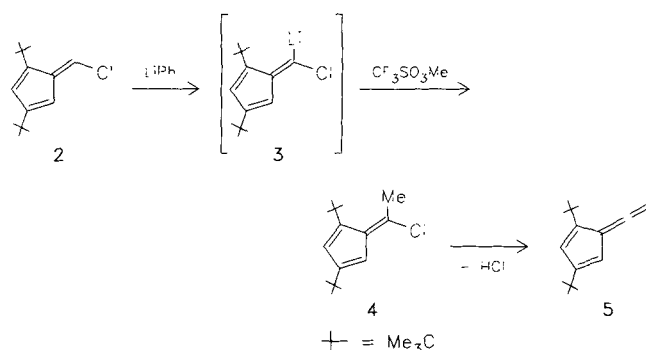


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 [16] In this procedure, LiOrBu also is present. However, BuNa and BuK can be obtained pure by filtration and washing [14]; suspension in hexane/TMEDA and hydrogenation gives LiOrBu-free NaH and KH. However, these reagents are less reactive and offer no preparative advantages.



pentafulvene partial structure (**1A**) or two pentalene units (**1B**). According to  $\pi$ -SCF-MO calculations the perimeter of **1** should exhibit a pronounced double-bond fixation determined by a pseudo-Jahn-Teller effect and the  $\pi$ -bonding isomer **1A** ( $C_s$  symmetry) should be ca. 4 kcal·mol<sup>-1</sup> lower in energy than **1B** ( $C_{2h}$  symmetry) with two overlapping pentalenoid partial structures. The delocalized 14 $\pi$ -electron system should have an enthalpy of formation ca. 14 kcal mol<sup>-1</sup> higher than that of **1A**.<sup>[1a]</sup>

For the synthesis of the tetra-*tert*-butyl derivative **11** of the tetracycle **1** we used 1,3-di-*tert*-butyl-5-vinylidenecyclopentadiene **5** as educt. While "pentafulveneallenes" were hitherto only accessible from diradical generators by pyrolysis or photolysis,<sup>[4]</sup> we prepared **5** in 88% yield as pale yellow crystals of m.p. 43-44°C (after sublimation) by



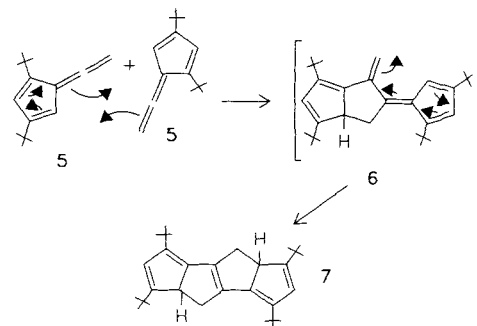
## Synthesis of a Dicyclopenta[*a,e*]pentalene by [6 + 2]-Cycloaddition of 1,3-Di-*tert*-butyl-5-vinylidenecyclopentadiene and Consecutive 8 $\pi$ -Electrocyclic Reaction\*\*

By Bernd Stowasser and Klaus Hafner\*

Dedicated to Professor Heinz A. Staab on the occasion of his 60th birthday

Nonbenzenoid linear annelated [4*n* + 2]- and [4*n*]- $\pi$ -electron systems can be formally regarded as annulenes perturbed by central  $\sigma$ -bonds. According to quantum chemical investigations the bonding behavior of these polycycles should be determined by the  $\pi$ -perimeter as well as by its partial structures.<sup>[1]</sup> Only three examples of linear annelated hydrocarbons containing more than two exclusively nonbenzenoid rings have so far been reported, namely cyclohepta[*a*]cyclopenta[*e*]- and cyclohepta[*a*]cyclopenta[*g*]azulene as well as azuleno[2,1-*a*]azulene.<sup>[2]</sup> The partial structures of these aromatic 18 $\pi$ -electron systems also contain [4*n* + 2]- $\pi$ -electrons.<sup>[3]</sup> Consequently, the bonding situation in a representative of the hitherto unknown systems with [4*n* + 2]-perimeter having [4*n*]- $\pi$ -partial structures is of special interest. These prerequisites are fulfilled by dicyclopenta[*a,e*]pentalene **1**. We report here on the synthesis

metalation of the 6-chloropentafulvene **2**<sup>[5]</sup> with phenyllithium (tetrahydrofuran (THF), -78°C) to the carbenoid **3**, followed by methylation with methyl trifluoromethanesulfonate (-78°C) to give **4** (yellow leaflets, m.p. 71°C, yield 33%) and subsequent HCl elimination with lithium 2,2,6,6-tetramethylpiperide (LiTMP) (-78 to 25°C).<sup>[6]</sup> **5** dimerizes in a solid-state reaction at ca. 10°C within approx. 14 days to give 1,3,5,7-tetra-*tert*-butyl-4,4a,8,8a-tetrahydrodicyclopenta[*a,e*]pentalene **7** (from *n*-hexane, pale-



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[\*\*] This work was supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Dr.-Otto-Röhm-Gedächtnisstiftung.

yellow crystals, decomp. above 114°C; yield 35%). The formation of **7** could involve a [6+2]-cycloaddition of the terminal bond of **5** to the pentafulvene moiety of a second molecule of **5** to give the tetrahydropentalene derivative **6**, which subsequently undergoes an 8 $\pi$ -electrocyclization to **7**.

Whereas the direct dehydrogenation of **7** with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in ether at 25°C affords only **8** (from *n*-hexane, brown crystals, sublimation >250°C; yield 63%),<sup>[7]</sup> the proton-catalyzed tautomerization (CHCl<sub>3</sub>/HCl, 25°C) of **7** leads to the hydro-

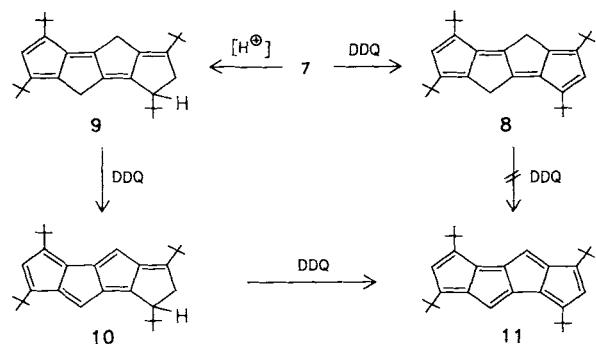


Table 1. Spectral data of **4**, **5**, **7**–**14**. <sup>1</sup>H-NMR at 300 MHz, *J* in Hz.

**4**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 1.15 (s; 9H, *t*Bu), 1.31 (s; 9H, *t*Bu), 2.71 (s; CH<sub>3</sub>), 6.26 (d, *J* = 2.4; 1H, 2-H or 4-H), 6.28 (d, *J* = 2.4; 1H, 2-H or 4-H); UV (*n*-hexane):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 260 (4.19) sh, 266 (4.27), 272 (4.27), 281 (4.06) sh, 376 nm (2.66)

**5**: <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.16 (s; 9H, *t*Bu), 1.36 (s; 9H, *t*Bu), 4.81 (d, *J* = 1.2; 2H, CH<sub>2</sub>), 6.04 (d, *J* = 2.0; 1H, 2-H), 6.24 (dt, *J*<sub>1</sub> = 2.0, *J*<sub>2</sub> = 1.2; 1H, 4-H); <sup>13</sup>C-NMR (C<sub>6</sub>D<sub>6</sub>, 75.47 MHz):  $\delta$  = 29.6, 31.4 (C(CH<sub>3</sub>)<sub>3</sub>), 32.3, 34.0 (C(CH<sub>3</sub>)<sub>3</sub>), 76.3 (CH<sub>2</sub>), 110.2 (C<sub>quart</sub>), 116.2 (C<sub>tert</sub>), 124.1 (C<sub>tert</sub>), 149.8 (C<sub>quart</sub>), 153.0 (C<sub>quart</sub>), 211.1 (C<sub>quart</sub>); UV (*n*-hexane):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 250 (4.13), 354 nm (2.80)

**7**: <sup>1</sup>H-NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  = 1.16 (s; 18H, *t*Bu), 1.33 (s; 18H, *t*Bu), 2.65 (m, *J*<sub>1</sub> = 12.5, *J*<sub>2</sub> = 5.8; 2H, 4/8-H), 3.25 (m, *J*<sub>1</sub> = 12.5, *J*<sub>2</sub> = 7.5; 2H, 4/8-H), 4.35 (ddd, *J*<sub>1</sub> = 7.5, *J*<sub>2</sub> = 5.8, *J*<sub>3</sub> = 1.8; 2H, 4a/8a-H), 6.38 (d, *J* = 1.8; 2H, 2/6-H); UV (*n*-hexane):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 227 (4.09), 276 (3.44), 392 nm (4.19)

**8**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 1.24 (s; 18H, *t*Bu), 1.26 (s; 18H, *t*Bu), 3.56 (s; 4H, 4/8-H), 6.36 (s; 2H, 2/6-H); UV (*n*-hexane):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 255 (3.36), 264 (3.37), 305 (3.79) sh, 320 (4.14) sh, 333 (4.46), 350 (4.68), 368 (4.64), 474 nm (3.24)

**9**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 0.96 (s; 9H, *t*Bu), 1.22 (s; 9H, *t*Bu), 1.26 (s; 9H, *t*Bu), 1.29 (s; 9H, *t*Bu), 2.68 (m; 2H, 2/3-H), 2.87 (dd, *J*<sub>1</sub> = 18.0, *J*<sub>2</sub> = 7.5; 1H, 2-H), 3.25 (d, *J* = 21.0; 1H, 4-H), 3.39 (d, *J* = 21.0; 1H, 4-H), 3.42 (s; 2H, 8-H), 6.34 (s; 1H, 6-H); UV (*n*-hexane):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 244 (3.63) sh, 252 (3.70), 260 (3.69), 288 (3.62) sh, 302 (3.71) sh, 358 (4.46) sh, 369 (4.53), 382 (4.46) sh, 425 nm (3.28) sh

**10**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 0.88 (s; 9H, *t*Bu), 1.18 (s; 9H, *t*Bu), 1.20 (s; 9H, *t*Bu), 1.22 (s; 9H, *t*Bu), 2.66 (dd, *J*<sub>1</sub> = 6.5, *J*<sub>2</sub> = 1.8; 1H, 3-H), 2.72 (dd, *J*<sub>1</sub> = 19.0, *J*<sub>2</sub> = 1.8; 1H, 2-H), 2.95 (dd, *J*<sub>1</sub> = 19.0, *J*<sub>2</sub> = 6.5; 1H, 2-H), 5.96 (br. s; 1H, 6-H or 8-H), 6.16 (s; 1H, 6-H or 8-H), 6.60 (d, *J* = 0.6; 1H, 4-H); UV (*n*-hexane):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 275 (3.97) sh, 327 (4.68), 337 (4.63) sh, 435 (3.33), 497 nm (3.04) sh

**11**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 1.31 (s; 18H, *t*Bu), 1.33 (s; 18H, *t*Bu), 6.58 (s; 2H, 2/6-H or 4/8-H), 6.72 (s; 2H, 2/6-H or 4/8-H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75.47 MHz):  $\delta$  = 29.8, 30.8 (C(CH<sub>3</sub>)<sub>3</sub>), 32.7, 33.5 (C(CH<sub>3</sub>)<sub>3</sub>), 118.3 (C<sub>tert</sub>), 134.3 (C<sub>quart</sub>), 137.3 (C<sub>tert</sub>), 142.7, 142.9, 145.8, 155.5 (C<sub>quart</sub>); UV (*n*-hexane):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 226 (4.10), 249 (3.92) sh, 349 (4.58), 399 (3.68) sh, 518 (3.25), 808 nm (1.57) sh

**12**: <sup>1</sup>H-NMR (CDCl<sub>3</sub>):  $\delta$  = 1.13 (s; 9H, *t*Bu), 1.44 (s; 9H, *t*Bu), 1.58 (s; 18H, *t*Bu), 3.70 (d, *J* = 1.9; 1H, 1-H), 7.42 (d, *J* = 1.9; 1H, 2-H), 7.70 (br. s; 1H, 6-H), 8.09 (s; 1H, 8-H), 8.46 (d, *J* = 0.8; 1H, 4-H); UV (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (lg  $\epsilon$ ) = 265 (3.83) sh, 308 (4.06), 369 (4.26), 435 (3.84) sh, 470 (3.50) sh, 547 (2.97) sh, 572 (3.06) sh, 622 (3.33) sh, 663 (3.43), 722 (3.24) sh, 862 (2.54), 974 nm (2.23)

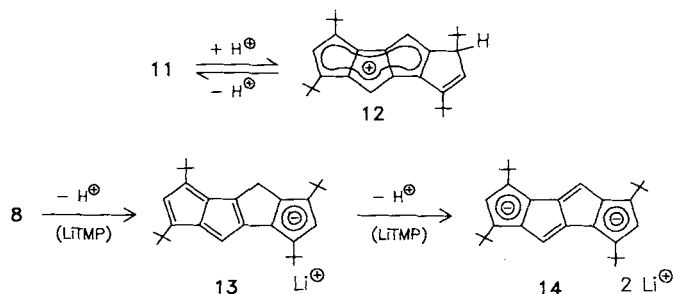
**13**: <sup>1</sup>H-NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.01 (s; 9H, *t*Bu), 1.03 (s; 9H, *t*Bu), 1.20 (s; 9H, *t*Bu), 1.22 (s; 9H, *t*Bu), 3.51 (s; 2H, 4-H), 4.42 (s; 1H, 8-H), 5.06 (s; 1H, 2-H), 5.65 (s; 1H, 6-H)

**14**: <sup>1</sup>H-NMR ([D<sub>8</sub>]THF):  $\delta$  = 1.00–1.33 (*t*Bu signals masked by LiTMP/TMP signals), 4.64 (s; 2H, 4/8-H or 2/6-H), 5.13 (s; 2H, 2/6-H or 4/8-H)

carbon **9** (from *n*-hexane, reddish-brown fine crystals, m.p. 182°C; yield 75%). Dehydrogenation with DDQ in the molar ratio 1:1 affords the dihydro compound **10** (greenish-brown powder, m.p. 131°C; yield 72%). Upon further dehydrogenation of **10** or reaction of **9** with DDQ in the molar ratio 1:2, the desired 1,3,5,7-tetra-*tert*-butyldicyclopenta[*a,e*]pentalene **11** is obtained as thermally stable brownish-violet crystals (chromatography on Al<sub>2</sub>O<sub>3</sub> BII–III with pentane) of m.p. 136°C (decomp.) in 70% yield.

Consistent with what was to be expected on the basis of quantum mechanical calculations, the ring-proton signals at  $\delta$  = 6.58 and 6.72 (in CDCl<sub>3</sub>) in the <sup>1</sup>H-NMR spectrum of **11** are shifted markedly upfield compared to those of bridged [14]annulenes such as *trans*-10b,10c-dihydropyrene<sup>[8]</sup> ( $\delta$  = 7.98–8.67) or *syn*-1,6:8,13-bismethano[14]annulene<sup>[9]</sup> ( $\delta$  = 7.1–7.9). In comparison to the ring-proton signals of 1,3,5-tri-*tert*-butylpentalene<sup>[10]</sup> ( $\delta$  = 4.72–5.07) the <sup>1</sup>H-signals of **11** are shifted to lower field. The similarity of the ring-proton signals of **10** and **11** (Table 1) reflects the cyclopolyolefin character (extensive double-bond fixation) of the new hydrocarbon **11**. The absorptions in the electronic spectrum of **11** (Table 1) correspond favorably to the singlet electron transfers calculated by Lindner<sup>[1a,11]</sup> and by Toyota and Nakajima<sup>[1b]</sup> for **1A** with localized double bonds.

**11** can be reversibly converted by protonation with trifluoroacetic acid in CHCl<sub>3</sub> at 25°C into the stable green cation **12**,<sup>[12]</sup> whose <sup>1</sup>H-NMR data are consistent with a



delocalized 10 $\pi$ -electron system. Deprotonation of **8** with equimolar amounts of LiTMP in THF at 25°C affords the lithium salt of the deep-green anion **13**, which can be further deprotonated with LiTMP to give the brownish-yellow dilithium salt of the 1,3,5,7-tetra-*tert*-butyldicyclopenta[*a,e*]pentalene dianion **14**. A comparison of the <sup>1</sup>H-NMR signals of the ring protons of **11** and **14** shows that the conversion of the 14 $\pi$ -perimeter into the 16 $\pi$ -electron system—taking into account the negative charges in **14**—does not lead to the formation of a clearly paratropic system (upfield shift:  $\Delta\delta$  = 1.5–2).<sup>[13]</sup>

Received: January 20, 1986 [Z 1630 1E]  
German version: *Angew. Chem.* 98 (1986) 477

CAS Registry numbers:

2, 85655-87-4; **3**, 101671-69-6; **4**, 101671-70-9; **5**, 101671-71-0; **7**, 101671-72-1; **8**, 101671-73-2; **9**, 101671-74-3; **10**, 101671-75-4; **11**, 101671-76-5; **12**, 101654-05-1; **13**, 101671-77-6; **14**, 101671-79-8.

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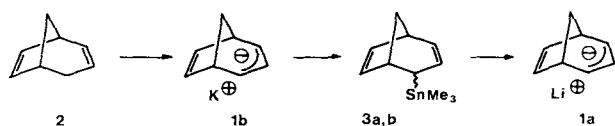
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- [6] All the compounds isolated gave correct elemental analyses.
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- [11] H. J. Lindner: Singlet electron transitions of **1A** calculated according to the  $\pi$ -SCF-CI method:  $\lambda_{\text{max}}(F)$ : 224 (0.210), 226 (0.151), 251 (0.031), 289 (0.040), 313 (0.009), 331 (1.045), 334 (0.479), 409 (0.199), 518 (0.003), 888 nm (0.003) ( $F$ =oscillator strength).
- [12] In addition to **12**, small amounts of the 3H tautomer are also formed.
- [13] In contrast to **14**, lithium-2,5-di-*tert*-butylcyclopenta[a]pentalenide [**3d**] shows a pronounced paratropic ring current.

## Bicyclo[3.2.1]octa-2,6-dienyllithium\*\*

By Norbert Hertkorn, Frank H. Köhler,\* Gerhard Müller, and Gabriele Reber

The bicyclo[3.2.1]octa-2,6-dienyl anion **1** is an illustrious example for uniting differently orientated chemists in their ambition to understand a molecule. Although the existence of **1** in solution was first demonstrated more than twenty years ago<sup>[1]</sup> a lithium derivative thereof has so far never been reported; indeed, no alkali metal derivative has ever been isolated. The central question since its discovery has been: Does **1** experience a stabilization due to bishomoaromaticity or not? Many careful and elegant experiments as well as different computational methods gave diametrically opposed answers (for reviews see Refs. [2–4]). During the last five years Grutzner and Jørgensen<sup>[2a]</sup> as well as Mayr, Schleyer et al.<sup>[2b]</sup> concluded from their calculations that homoaromaticity should be negligible in **1**. Modified computations by Brown et al.<sup>[2c]</sup> were much in favor of homoaromaticity. The same was deduced by Washburn<sup>[3]</sup> from the experimental acidities of bicyclo[3.2.1]octa-2,6-diene **2** and similar compounds. Christl et al.<sup>[4a]</sup> and our group<sup>[4b]</sup> have published  $^{13}\text{C-NMR}$  data which are in accord with (possibly slight) homoconjugation; at least, considerable charge transfer from the allylic to the olefinic part of **1** could be demonstrated. We have now been able to isolate the lithium derivative **1a** of the anion **1** as tetra-



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\*\*] This work was supported by the Fonds der Chemischen Industrie and BASF.

methylethylenediamine (TMEDA) complex **1c**, and to obtain  $^{13}\text{C-NMR}$  data of **1a**.

As described earlier,<sup>[4b]</sup> **2** was converted into the potassium derivative **1b** of the anion **1**. Reaction with  $\text{Me}_3\text{SnCl}$  furnished a mixture of *exo/endo*-4-trimethylstannylbicyclo[3.2.1]octa-2,6-dienes **3a/b**,<sup>[5]</sup> and these were transformed into **1a** by methyllithium. **1a**, which according to its  $^{13}\text{C-NMR}$  spectrum contained only small amounts of ether, was dissolved in various solvents in order to obtain the  $^{13}\text{C-NMR}$  data listed in Table 1; new data for **1b** are also listed. The number of signals and their shifts show that in solution the anion has the same symmetry in **1a** and **1b**. We also wanted to establish how the charge transfer from the allylic to the olefinic part of **1** changes when the equilibrium between contact ion pairs and solvent separated ion pairs<sup>[6]</sup> is influenced by different alkali ions and/or solvents. As can be seen from Table 1 the average chemical shift  $\delta^{\text{av}}$  is not constant. Hence the effect of the charge delocalization in the  $\pi$ -system on  $\delta(^{13}\text{C})$  is obscured by other effects like aggregation, participation of the  $\sigma$ -framework, and geometrical changes within **1**.

Table 1.  $^{13}\text{C-NMR}$  data [a] of **1a** and **1b** in various solvents [b].

Cpd.	Solvent	C3	C6/7	C2/4	C1/5	C8	$\delta^{\text{av}}$
<b>1a</b>	TMEDA	114.4	84.2	55.6	37.2	29.9	62.3
		<i>142</i>	<i>158</i>	<i>159</i>	<i>138</i>	<i>132</i>	
<b>1a</b>	Benzene	115.3	83.8	56.3	37.3	30.0	62.5
		<i>142</i>	<i>159</i>	<i>162</i>	<i>140</i>	<i>134</i>	
<b>1a</b>	$\text{Et}_2\text{O}$	114.9	83.0	55.3	36.9	29.4	61.8
		<i>142</i>	<i>159</i>	<i>162</i>	<i>140</i>	<i>134</i>	
<b>1a</b>	DME	114.9	85.6	56.2	37.8	30.3	63.1
		<i>142</i>	<i>158</i>	<i>162</i>	<i>137</i>	<i>131</i>	
<b>1a</b>	THF	117.6	90.1	58.1	38.8	31.3	65.4
		<i>141</i>	<i>158</i>	<i>158</i>	<i>135</i>	<i>131</i>	
<b>1a</b>	Dioxane	118.0	90.0	57.6	38.0	30.7	65.0
		<i>137</i>	<i>154</i>	<i>161</i>	<i>133</i>	<i>131</i>	
<b>1b</b>	DME	119.8	89.8	57.9	39.8	31.3	65.8
		<i>137</i>	<i>154</i>	<i>161</i>	<i>133</i>	<i>131</i>	
<b>1b</b> [c]	THF	119.5	90.0	57.9	39.8	31.4	65.8
		<i>138</i>	<i>157</i>	<i>161</i>	<i>134</i>	<i>131</i>	

[a] Shifts measured at 273 K (**1a** in  $\text{C}_6\text{H}_6$ ; 280 K, in dioxane; 288 K) relative to internal cyclohexane ( $\delta = 27.30$ ) and converted to the  $\delta$ -scale.  $^1\text{J}(^{13}\text{C}^1\text{H})$  in Hz is given in italics. Numbering scheme cf. Figure 1. Instrument: Bruker CXP 200. [b] TMEDA (tetramethylethylenediamine), DME (1,2-dimethoxyethane), THF (tetrahydrofuran). [c] Remeasured; the deviation from our earlier results [4b] is attributed to changes for the reference ( $\text{C}_6\text{H}_{12}$  instead of  $[\text{D}_8]\text{THF}$ ), the solvent (THF instead of  $[\text{D}_8]\text{THF}$ ), and different concentrations.

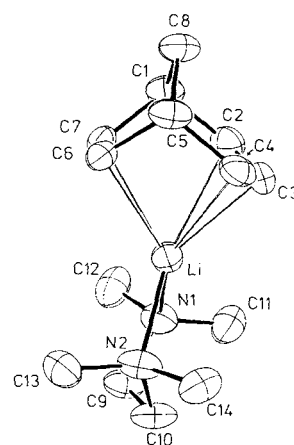


Fig. 1. Structure of bicyclo[3.2.1]octa-2,6-dienyllithium-TMEDA **1c** in the crystal (ORTEP, thermal ellipsoids 50%, hydrogens omitted). Important distances [Å] and angles [°]: C1-C2 1.520(4), C4-C5 1.517(5), C2-C3 1.394(5), C3-C4 1.384(4), C5-C6 1.508(5), C1-C7 1.512(4), C6-C7 1.354(4), C1-C8 1.542(4), C5-C8 1.538(4), Li-C2 2.515(6), Li-C4 2.440(6), Li-C3 2.194(6), Li-C6 2.399(5), Li-C7 2.429(6).