# CH<sub>3</sub>-Deprotonation of 9-Methylanthracene under Mild Conditions

# Nils Finkelmeier, Arne Visscher, Sebastian Wandtke, Regine Herbst-Irmer, and Dietmar Stalke\*<sup>a</sup>

#### **Supporting Information**

#### 1. Synthesis

9-Methylanthracene (2.0 g, 10.42 mmol) was dissolved in diethyl ether (40 mL) and cooled to  $-15^{\circ}$ C. Then TMEDA (2.41 g, 20.84 mmol) was added. To this mixture TMSMeLi (13.0 mL, 10.5 mmol, 0.80 m) was added over the course of 30 min. The reaction was stirred for 15 min until a black precipitate had formed. The precipitate was separated from the mother liquor by filtration with a cooled filtration device ( $-78^{\circ}$ C). The black solid was re-dissolved in pre-cooled THF (40 mL). The solution was concentrated to ca.20 mL and then stored at  $-30^{\circ}$ C for crystallization. For the NMR experiments 50 mg of 9-Methylanthracene and 60 mg of TMEDA were dissolved in THF  $d_8$  and reacted with one equivalent of TMSMeLi in an NMR tube at  $-15^{\circ}$ C. Yield > 95 % because the concentration of potential side products and the starting material remain below the NMR spectroscopic detection limit. CHN elemental analysis was attempted but failed due to the thermal instability of the product.

#### 2. NMR Data

#### <sup>1</sup>H-NMR

(THF *d*<sub>8</sub>, 300 MHz):

 $\delta$  [ppm] = 7.34 (d, J = 8.0 Hz, 2H, H<sub>1,8</sub>), 6.52 (m, 4H, H<sub>3,4,5,6</sub>), 6.04 (m, 2H, H<sub>27</sub>), 5.06 (s, 1H, H<sub>10</sub>), 4.12 (s, 2H, CH<sub>2</sub><sup>-</sup>).

#### <sup>7</sup>Li-NMR

(THF  $d_8$ , 194 MHz):  $\delta$  [ppm] = -2.30 (s).

# ${}^{13}C{}^{1}H}-NMR$

(THF *d*<sub>8</sub>, 126 MHz):

 $\delta$  [ppm] = 145.4 (2C, C<sub>8a,9a</sub>), 140.0 (2C, C<sub>4a,10a</sub>), 125.3 (2C, C<sub>4,5</sub>), 124.5 (2C, C<sub>1,8</sub>), 122.7 (2C, C<sub>3,6</sub>), 121.8 (1C, C<sub>9</sub>), 111.8 (2C, C<sub>2,7</sub>), 85.9 (1C, C<sub>10</sub>), 75.0 (1C, C15).



# 3. Crystallographic Data

Single crystals were selected from a Schlenk flask under argon atmosphere and covered with perfluorated polyether oil on a microscope slide, which was cooled with a nitrogen gas flow supplied by the X-TEMP2 device.<sup>1</sup> An appropriate crystal was selected using a polarizing microscope, fixed on the tip of a MiTeGen<sup>®</sup> MicroMount, transferred to a goniometer head, and shock cooled by the crystal cooling device. The data were collected from these shock-cooled crystals at 100(2) K. The data were measured on an Incoatec Mo microfocus source<sup>2</sup> (**1a**) and on a Bruker TXS Mo rotating anode (**1b**) both with Helios mirror optics and an APEX II detector at a D8 goniometer with Mo K<sub>a</sub> radiation,  $\lambda = 0.71073$  Å. The data were integrated with SAINT<sup>3</sup>, and multi-scan absorption correction (SADABS)<sup>4</sup> was applied. A 3  $\lambda$  correction<sup>5</sup> was applied with correction factors of 0.0086 (**1a**) and 0.0024 (**1b**), respectively. The structures were solved by direct methods (SHELXT)<sup>6</sup> and refined by full-matrix least-squares methods against  $F^2$  (SHELXL)<sup>7</sup> within the SHELXLE GUI.<sup>8</sup> All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms (beside those discussed below) were refined isotropically on calculated positions using a riding model with their  $U_{iso}$  values constrained to equal 1.5 times the  $U_{eq}$  of their pivot atoms for terminal sp<sup>3</sup> carbon atoms and 1.2 times for all other carbon atoms.

### Crystal structure of 1a:



Figure S1: Crystal structure of **1a**. The anisotropic displacement parameters are depicted at the 50 % probability level. The hydrogen atoms are omitted for clarity.

The crystals of compound **1a** diffract very weakly. Nearly all atoms of the TMEDA groups are disordered. The occupancies refined to 0.858(9):0.152(8) and 0.891(5):0.109(5) respectively. Both methylantracene molecules are disordered about the inversion centre leading to a 50:50 head-to tail disorder. Therefore, distance restraints for all chemically equivalent 1-2 and 1-3 distances and restraints for the anisotropic displacement parameters were used.

In spite of the poor resolution and the disorder the hydrogen atoms can be found in the residual density map.



Figure S2: Residual density around the two deprotonated methylantracene molecules

The residual density indicates deprotonation of the methyl group. The  $CH_2$  hydrogen atoms and the hydrogen at C(9) / C(24) were refined with distance restraints (SADI) and U(H) constrained to 1.2 times of Ueq(C). With this weak diffraction and disorder bond lengths should be discussed with care. But the derived bond lengths fit best to structure b and c in scheme 2:

C(1)-C(2)	C(16)-C(17)	
C(2)-C(3)	C(17)-C(18)	
C(2)-C(15)	C(17)-C(30)	
C(3)-C(4)	C(18)-C(23)	
C(3)-C(8)	C(18)-C(19)	
C(4)-C(5)	C(19)-C(20)	
C(5)-C(6)	C(20)-C(21)	
C(6)-C(7)	C(21)-C(22)	
C(7)-C(8)	C(22)-C(23)	
C(8)-C(9)	C(23)-C(24)	
C(9)-C(10)	C(24)-C(25)	
C(10)-C(15)	C(25)-C(30)	
C(10)-C(11)	C(25)-C(26)	
C(11)-C(12)	C(26)-C(27)	
C(12)-C(13)	C(27)-C(28)	
C(13)-C(14)	C(28)-C(29)	
C(14)-C(15)	C(29)-C(30)	

Crystal for compound **1b** diffract better, but unfortunately again the two cations (occupancies 0.497(5): 0.503(5), 0.527(5): 0.473(5), 0.459(7): 0.541(7) and 0.577(4): 0.423(3), respectively) and two of the three methylantracene species (head-to-tail, occupancies 0.850(3): 0.150(3) and 0.779(4): 0.221(4), respectively) are disordered. Again distance restraints for all chemically equivalent 1-2 and 1-3 distances and restraints for the anisotropic displacement parameters were used.



Figure S3. Crystal structure of **1b**. The anisotropic displacement parameters are depicted at the 50 % probability level. The hydrogen atoms are omitted for clarity.

Additionally electroneutrality requires two deprotonated and one undeprotonated species. But here the residual density around the methyl group cannot distinguish the deprotonated and the undeprotonated species. Again, the bond lengths should be discussed with care. But for all three species they fit better to undeprotonated methylanthracene. So we assume that in all three positions there is a mixture of deprotoated and undeprotonated methylanthracene. Nevertheless, we refined disordered  $CH_3$  for one species and disordered  $CH_2$  for the others. But that should not be considered as a proof for  $CH_3$  or  $CH_2$ .





Figure S4: Residual density around the three methylantracene species

C(1)-C(2)	C(16)-C(17)	C(31)-C(32)
C(2)-C(3)	C(17)-C(18)	C(32)-C(33)
C(2)-C(15)	C(17)-C(30)	C(32)-C(45)
C(3)-C(4)	C(18)-C(23)	C(33)-C(34)
C(3)-C(8)	C(18)-C(19)	C(33)-C(38)
C(4)-C(5)	C(19)-C(20)	C(34)-C(35)
C(5)-C(6)	C(20)-C(21)	C(35)-C(36)
C(6)-C(7)	C(21)-C(22)	C(36)-C(37)
C(7)-C(8)	C(22)-C(23)	C(37)-C(38)
C(8)-C(9)	C(23)-C(24)	C(38)-C(39)
C(9)-C(10)	C(24)-C(25)	C(39)-C(40)
C(10)-C(11)	C(25)-C(26)	C(40)-C(41)
C(10)-C(15)	C(25)-C(30)	C(40)-C(45)
C(11)-C(12)	C(26)-C(27)	C(41)-C(42)
C(12)-C(13)	C(27)-C(28)	C(42)-C(43)
C(13)-C(14)	C(28)-C(29)	C(43)-C(44)
C(14)-C(15)	C(29)-C(30)	C(44)-C(45)

Identification code	1a	1b
CCDC No	1452372	1452373
Empirical formula	C <sub>27</sub> H <sub>43</sub> LiN <sub>4</sub>	$C_{69}H_{98}Li_2N_8$
Formula weight [g/mol]	430.59	1053.43
Temperature [K]	100(2)	100(2)
Wavelength [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_{l}/c$	$P2_{1}/n$
<i>a</i> [Å]	16.526(2)	9.486(2)
<i>b</i> [Å]	9.874(2)	34.841(3)
<i>c</i> [Å]	18.038(3)	19.391(2)
β [°]	115.24(2)	93.77(2)
Volume [Å <sup>3</sup> ]	2662.4(9)	6394.9(16)
Z	4	4
$ ho_{ m calc}  [{ m Mg}/{ m m}^3]$	1.074	1.094
μ [mm <sup>-1</sup> ]	0.063	0.064
F(000)	944	2296
Crystal size [mm <sup>3</sup> ]	0.06 x 0.08 x 0.3	0.2 x 0.2 x 0.3
Θ range [°]	1.362 to 25.023	1.169 to 28.741
Reflections collected	38087	124098
Independent reflections	4639	16530
R(int)	0.0926	0.0445
Completeness to $\Theta_{\text{max}}$	98.7%	99.9 %
Absorption correction	Multi-scan	Multi-Scan
Max. / min. transmission	0.7446 / 0.6486	0.8621 / 0.8065
Restraints / parameters	1328 / 523	4746 / 1275
GooF	1.060	1.032
<i>R</i> 1 / <i>wR</i> 2 (I>2σ(I))	0.0839 / 0.1690	0.0545 / 0.1466
R1 / wR2 (all data)	0.1732 / 0.2106	0.0703 / 0.1595
Diff. peak and hole [eÅ-3]	0.198 and -0.189	0.288 and -0.215

Table S1. Crystallographic data for 1a and 1b.

1. a) T. Kottke, D. Stalke, J. Appl. Crystallogr., 1993, 26, 615-619; b) T. Kottke, R. J. Lagow, D. Stalke, J. Appl. Crystallogr., 1996, 29, 465-468; c) D. Stalke, Chem. Soc. Rev., 1998, 27, 171-178.

5

- 2. T. Schulz, K. Meindl, D. Leusser, D. Stern, J. Graf, C. Michaelsen, M. Ruf, G. M. Sheldrick and D. Stalke, J. Appl. Crystallogr., 2009, 42, 885-891.
- 3. SAINT v7.68A in Bruker APEX v2011.9, Bruker AXS Inst. Inc., Madison, USA, 2008.
- 4. L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, J. Appl. Crystallogr., 2015, 48, 3-10.
- 5. L. Krause, R. Herbst-Irmer, D. Stalke, J. Appl. Crystallogr., 2015, 48, 1907-1913.
- 6. G. M. Sheldrick, Acta Crystallogr., Section A, 2015, 71, 3-8.
- 7. G. M. Sheldrick, Acta Crystallogr., Section C, 2015, 71, 3-8.
- 8. C. B. Hübschle, G. M. Sheldrick and B. Dittrich, J. Appl. Cryst., 2011, 44, 1281-1284.