Supplementary Material/Organic Letters

The Solution and Solid State Structure of (1-Methoxy-8-naphthyllithium·THF)$_2$

Jürgen Betz, Frank Hampel, and Walter Bauer*

Instiut für Organische Chemie, Universität Erlangen-Nürnberg,
Henkestrasse 42, D-91054 Erlangen, Germany

bauer@organik.uni-erlangen.de

^{13}C NMR Measurement: The ^{13}C spectrum was obtained on a JEOL GX400 spectrometer (100.5 MHz for ^{13}C). To enhance resolution a Gaussian window function was applied. To avoid decomposition of the moisture sensitive lithium compound, the sample was prepared in an NMR tube sealed with a serum cap. 0.25 ml (6.3 mmol) *n*-BuLi (2.5M solution in hexane) was added to the 1-methoxynaphthalene (0.6 mmol). The solvent was removed *in vacuo* and 0.7 ml THF-d_8 were added. After 8 h at room temperature the metalation was completed and the spectrum was recorded.

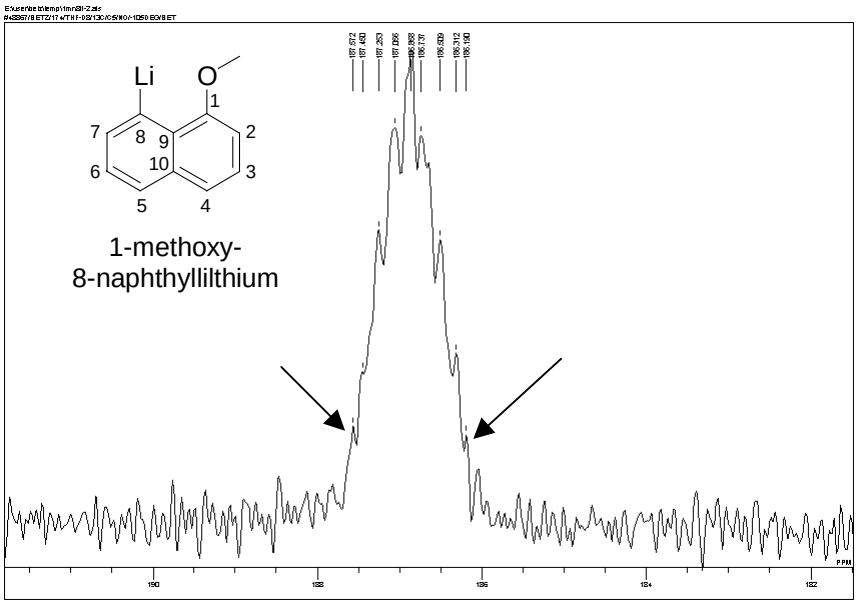

Figure1. ^{13}C spectrum of (1-methoxy-8-naphthyllithium·THF)$_2$ in THF-d_8 at –105°C. Shown is the zoomed region around the carbon atom C8 with its ^{1}J(^{13}C,^{7}Li) couplings. The peaks marked by arrows are noise artifacts what can be shown by the coupling constants: the average distance between two peaks is about 19.3 Hz whereas the marked peaks are only about 10 Hz separated from the neighboring peaks.

X-ray: The X-ray data were collected on a Nonius Kappa CCD. All relevant data are given in Tables 1-5

Table 1. Crystal data and structure refinement for jub01_2.

Identification code	jub01_2
Empirical formula	C15 H17 Li O2
Formula weight	236.23
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic

Space group	P2(1)/n	
Unit cell dimensions	a = 8.1816(5) Å	α= 90°.
	b = 21.9649(14) Å	β= 117.969(3)°.
	c = 8.2345(3) Å	γ = 90°.
Volume	1306.97(12) $Å^3$	
Z	4	
Density (calculated)	1.201 Mg/m^3	
Absorption coefficient	0.077 mm^{-1}	
F(000)	504	
Crystal size	0.35 x 0.30 x 0.30 mm^3	
Theta range for data collection	6.89 to 27.58°.	
Index ranges	-10<=h<=10, -28<=k<=26, -10<=l<=10	
Reflections collected	5020	
Independent reflections	2914 [R(int) = 0.0489]	
Reflections [I>2sig.(I)]	1841	
Completeness to theta = 27.58°	96.2 %	
Max. and min. transmission	0.9774 and 0.9737	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2914 / 0 / 163	
Goodness-of-fit on F^2	1.402	
Final R indices [I>2sigma(I)]	R1 = 0.0701, wR2 = 0.1748	
R indices (all data)	R1 = 0.1173, wR2 = 0.1906	
Largest diff. peak and hole	0.587 and -0.523 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for jub01_2. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Li(1)	6028(6)	-234(2)	1430(5)	32(1)
C(1)	8080(3)	890(1)	2851(3)	28(1)
C(2)	9513(3)	1289(1)	3702(3)	38(1)
C(3)	9156(4)	1887(1)	4070(4)	46(1)
C(4)	7407(4)	2070(1)	3596(4)	42(1)
C(5)	4075(4)	1841(1)	2260(3)	37(1)
C(6)	2645(4)	1445(1)	1393(3)	37(1)
C(7)	2979(3)	855(1)	938(3)	31(1)
C(8)	4711(3)	629(1)	1325(3)	27(1)
C(9)	6195(3)	1058(1)	2281(3)	27(1)
O(10)	8326(2)	290(1)	2492(2)	32(1)
C(10)	5898(3)	1665(1)	2717(3)	32(1)
O(20)	5741(2)	-874(1)	2916(2)	35(1)
C(21)	5648(4)	-1514(1)	2513(4)	39(1)
C(22)	3674(4)	-1713(1)	1925(5)	52(1)
C(23)	2778(4)	-1165(1)	2349(4)	50(1)
C(24)	4403(4)	-771(1)	3556(4)	40(1)
C(30)	10173(3)	94(1)	3011(3)	39(1)

Table 3. Bond lengths [Å] and angles [°] for jub01_2.

Li(1)-O(20)	1.949(4)
Li(1)-O(10)	2.020(4)
Li(1)-C(8)	2.162(5)
Li(1)-C(8)#1	2.232(4)
Li(1)-Li(1)#1	2.391(8)
C(1)-C(2)	1.366(3)
C(1)-O(10)	1.385(3)
C(1)-C(9)	1.434(3)
C(2)-C(3)	1.409(4)
C(3)-C(4)	1.356(4)
C(4)-C(10)	1.415(3)
C(5)-C(6)	1.360(4)
C(5)-C(10)	1.411(3)
C(6)-C(7)	1.413(3)
C(7)-C(8)	1.389(3)
C(8)-C(9)	1.444(3)
C(8)-Li(1)#1	2.232(4)
C(9)-C(10)	1.430(3)
O(10)-C(30)	1.431(3)
O(20)-C(21)	1.437(3)
O(20)-C(24)	1.439(3)
C(21)-C(22)	1.517(4)
C(22)-C(23)	1.532(4)
C(23)-C(24)	1.506(4)

O(20)-Li(1)-O(10)	120.1(2)
O(20)-Li(1)-C(8)	116.9(2)
O(10)-Li(1)-C(8)	82.14(16)
O(20)-Li(1)-C(8)#1	107.60(19)
O(10)-Li(1)-C(8)#1	114.53(19)
C(8)-Li(1)-C(8)#1	114.11(18)
O(20)-Li(1)-Li(1)#1	133.8(3)
O(10)-Li(1)-Li(1)#1	105.3(2)
C(8)-Li(1)-Li(1)#1	58.45(17)
C(8)#1-Li(1)-Li(1)#1	55.66(16)
C(2)-C(1)-O(10)	123.0(2)
C(2)-C(1)-C(9)	122.3(2)

O(10)-C(1)-C(9)	114.65(19)
C(1)-C(2)-C(3)	119.7(2)
C(4)-C(3)-C(2)	120.8(2)
C(3)-C(4)-C(10)	120.6(2)
C(6)-C(5)-C(10)	120.5(2)
C(5)-C(6)-C(7)	120.0(2)
C(8)-C(7)-C(6)	124.8(2)
C(7)-C(8)-C(9)	113.5(2)
C(7)-C(8)-Li(1)	139.2(2)
C(9)-C(8)-Li(1)	105.90(19)
C(7)-C(8)-Li(1)#1	98.32(17)
C(9)-C(8)-Li(1)#1	124.45(18)
Li(1)-C(8)-Li(1)#1	65.89(18)
C(10)-C(9)-C(1)	116.2(2)
C(10)-C(9)-C(8)	123.1(2)
C(1)-C(9)-C(8)	120.7(2)
C(1)-O(10)-C(30)	117.44(18)
C(1)-O(10)-Li(1)	115.79(18)
C(30)-O(10)-Li(1)	126.63(18)
C(5)-C(10)-C(4)	121.6(2)
C(5)-C(10)-C(9)	118.1(2)
C(4)-C(10)-C(9)	120.4(2)
C(21)-O(20)-C(24)	105.78(18)
C(21)-O(20)-Li(1)	124.71(18)
C(24)-O(20)-Li(1)	116.90(18)
O(20)-C(21)-C(22)	106.8(2)
C(21)-C(22)-C(23)	104.6(2)
C(24)-C(23)-C(22)	103.6(2)
O(20)-C(24)-C(23)	104.8(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for jub01_2. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Li(1)	35(2)	27(2)	33(2)	1(2)	16(2)	-1(2)
C(1)	32(1)	23(1)	29(1)	1(1)	14(1)	-2(1)
C(2)	30(1)	34(1)	46(1)	0(1)	14(1)	-6(1)
C(3)	44(2)	32(2)	52(2)	-7(1)	13(1)	-14(1)
C(4)	52(2)	23(1)	45(2)	-5(1)	19(1)	-4(1)
C(5)	49(2)	26(1)	39(1)	2(1)	23(1)	10(1)
C(6)	36(1)	38(2)	41(1)	6(1)	22(1)	11(1)
C(7)	31(1)	31(1)	32(1)	-1(1)	15(1)	-3(1)
C(8)	31(1)	25(1)	29(1)	1(1)	17(1)	-1(1)
C(9)	33(1)	23(1)	27(1)	2(1)	15(1)	-1(1)
O(10)	27(1)	28(1)	40(1)	-2(1)	15(1)	2(1)
C(10)	42(1)	21(1)	32(1)	2(1)	17(1)	1(1)
O(20)	41(1)	26(1)	44(1)	3(1)	24(1)	-1(1)
C(21)	40(2)	27(1)	50(2)	5(1)	22(1)	3(1)
C(22)	47(2)	40(2)	71(2)	-10(1)	30(1)	-7(1)
C(23)	42(2)	50(2)	62(2)	-2(1)	28(1)	4(1)
C(24)	52(2)	35(1)	44(1)	0(1)	31(1)	0(1)
C(30)	30(1)	43(2)	44(1)	0(1)	18(1)	5(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^{3}) for jub01_2.

	x	y	z	U(eq)
H(2A)	10744	1164	4045	46
H(3A)	10153	2165	4656	56
H(4A)	7192	2475	3858	50
H(5A)	3844	2238	2560	45
H(6A)	1421	1566	1093	44
H(7A)	1945	592	323	37
H(21A)	6521	-1743	3616	46
H(21B)	5974	-1588	1514	46
H(22A)	3651	-2076	2627	62
H(22B)	3024	-1811	596	62
H(23A)	1928	-949	1208	60
H(23B)	2083	-1294	3003	60
H(24A)	4037	-336	3425	48
H(24B)	4908	-889	4863	48
H(30D)	11017	442	3485	58
H(30C)	10228	-75	1937	58
H(30B)	10540	-218	3968	58