Crystallographic Information for

Alkoxyboration: Ring-Closing Addition of B–O σ Bonds Across Alkynes

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X-ray Data Collection, Structure Solution and Refinement for **4b**.

A colorless crystal of approximate dimensions 0.311 x 0.174 x 0.122 mm was mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space group *Pbcn* that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques.[5] The analytical scattering factors[6] for neutral atoms were used throughout the analysis. There was half of an acetone solvent molecule present per formula-unit (hydrogen atoms were included using a riding model). All other hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}).

At convergence, wR2 = 0.1002 and Goof = 1.025 for 319 variables refined against 4734 data (0.73 Å), R1 = 0.0407 for those 3950 data with $I > 2.0\sigma(I)$.

References.

1. APEX2 Version 2013.6-2, Bruker AXS, Inc.; Madison, WI 2013.
2. SAINT Version 8.32b, Bruker AXS, Inc.; Madison, WI 2013.
3. Sheldrick, G. M. SADABS, Version 2008/1, Bruker AXS, Inc.; Madison, WI 2007.
4. Sheldrick, G. M. SHELXTL, Version 2008/4, Bruker AXS, Inc.; Madison, WI 2008.
5. Sheldrick, G. M. SHELXL-2013/3, Bruker AXS, Inc.; Madison, WI 2013.
6. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

Definitions:

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

Table 1. Crystal data and structure refinement for **4b**.

Identification code	sab12 (Josh Hirner)	
Empirical formula	$C_{19}H_{16}BNO_5 \bullet ½ (C_3H_6O)$	
Formula weight	378.18	
Temperature	83(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	*Pbcn*	
Unit cell dimensions	a = 6.6172(3) Å	α= 90°.
	b = 15.1115(7) Å	β= 90°.
	c = 37.1855(18) Å	γ = 90°.
Volume	3718.4(3) $Å^3$	
Z	8	
Density (calculated)	1.351 Mg/m^3	
Absorption coefficient	0.097 mm^{-1}	
F(000)	1584	
Crystal color	colorless	
Crystal size	0.311 x 0.174 x 0.122 mm^3	
Theta range for data collection	2.191 to 29.136°	
Index ranges	$-9 \le h \le 8$, $-20 \le k \le 20$, $-50 \le l \le 50$	
Reflections collected	29859	
Independent reflections	4734 [R(int) = 0.0301]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8622 and 0.8140	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4734 / 0 / 319	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I) = 3950 data]	R1 = 0.0407, wR2 = 0.0942	
R indices (all data, 0.73 Å)	R1 = 0.0516, wR2 = 0.1002	
Largest diff. peak and hole	0.478 and -0.267 $e.Å^{-3}$	

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

	x	y	z	U(eq)
B(1)	892(2)	1174(1)	1488(1)	13(1)
N(1)	2525(2)	651(1)	1756(1)	13(1)
O(1)	401(1)	527(1)	495(1)	16(1)
O(2)	-1066(1)	948(1)	1652(1)	16(1)
O(3)	-2361(1)	238(1)	2127(1)	20(1)
O(4)	1380(1)	2114(1)	1564(1)	17(1)
O(5)	3481(2)	2962(1)	1886(1)	25(1)
C(1)	1993(2)	1106(1)	480(1)	15(1)
C(2)	2978(2)	1356(1)	167(1)	18(1)
C(3)	4588(2)	1939(1)	208(1)	21(1)
C(4)	5151(2)	2250(1)	549(1)	21(1)
C(5)	4126(2)	1986(1)	858(1)	18(1)
C(6)	2494(2)	1399(1)	824(1)	14(1)
C(7)	1078(2)	973(1)	1071(1)	13(1)
C(8)	-100(2)	453(1)	856(1)	14(1)
C(9)	-1748(2)	-185(1)	913(1)	14(1)
C(10)	-3431(2)	-169(1)	684(1)	17(1)
C(11)	-4927(2)	-811(1)	714(1)	19(1)
C(12)	-4757(2)	-1475(1)	972(1)	19(1)
C(13)	-3107(2)	-1490(1)	1202(1)	19(1)
C(14)	-1603(2)	-852(1)	1173(1)	17(1)
C(15)	-935(2)	449(1)	1945(1)	14(1)
C(16)	1206(2)	154(1)	2013(1)	16(1)
C(17)	2863(2)	2244(1)	1797(1)	18(1)
C(18)	3691(2)	1378(1)	1935(1)	23(1)
C(19)	3903(2)	30(1)	1562(1)	18(1)
O(6)	0	1849(1)	2500	30(1)
C(20)	0	2642(1)	2500	24(1)
C(21)	1443(4)	3144(2)	2727(1)	71(1)

Table 3. Bond lengths [Å] and angles [°] for **4b**.

B(1)-O(2)	1.4732(16)
B(1)-O(4)	1.4831(16)
B(1)-C(7)	1.5838(17)
B(1)-N(1)	1.6694(16)
N(1)-C(19)	1.4942(15)
N(1)-C(16)	1.4960(16)
N(1)-C(18)	1.4991(16)
O(1)-C(1)	1.3705(15)
O(1)-C(8)	1.3885(14)
O(2)-C(15)	1.3276(14)
O(3)-C(15)	1.2040(15)
O(4)-C(17)	1.3222(16)
O(5)-C(17)	1.2072(15)
C(1)-C(2)	1.3845(17)
C(1)-C(6)	1.3954(16)
C(2)-C(3)	1.3907(19)
C(3)-C(4)	1.4024(19)
C(4)-C(5)	1.3928(18)
C(5)-C(6)	1.4034(18)
C(6)-C(7)	1.4612(16)
C(7)-C(8)	1.3657(17)
C(8)-C(9)	1.4709(17)
C(9)-C(14)	1.4013(17)
C(9)-C(10)	1.4021(17)
C(10)-C(11)	1.3902(18)
C(11)-C(12)	1.3925(19)
C(12)-C(13)	1.3881(19)
C(13)-C(14)	1.3889(18)
C(15)-C(16)	1.5070(17)
C(17)-C(18)	1.5094(18)
O(6)-C(20)	1.198(2)
C(20)-C(21)#1	1.483(2)
C(20)-C(21)	1.483(2)

O(2)-B(1)-O(4)	109.50(10)
O(2)-B(1)-C(7)	115.46(10)
O(4)-B(1)-C(7)	110.74(10)
O(2)-B(1)-N(1)	102.20(9)
O(4)-B(1)-N(1)	101.44(9)
C(7)-B(1)-N(1)	116.32(10)
C(19)-N(1)-C(16)	110.39(9)
C(19)-N(1)-C(18)	111.16(10)
C(16)-N(1)-C(18)	112.59(10)
C(19)-N(1)-B(1)	113.85(9)
C(16)-N(1)-B(1)	104.01(9)
C(18)-N(1)-B(1)	104.59(9)
C(1)-O(1)-C(8)	105.92(9)
C(15)-O(2)-B(1)	114.53(9)
C(17)-O(4)-B(1)	115.38(10)
O(1)-C(1)-C(2)	124.74(11)
O(1)-C(1)-C(6)	110.34(10)
C(2)-C(1)-C(6)	124.92(12)
C(1)-C(2)-C(3)	116.29(12)
C(2)-C(3)-C(4)	120.86(12)
C(5)-C(4)-C(3)	121.40(12)
C(4)-C(5)-C(6)	118.87(12)
C(1)-C(6)-C(5)	117.66(11)
C(1)-C(6)-C(7)	106.57(11)
C(5)-C(6)-C(7)	135.76(11)
C(8)-C(7)-C(6)	104.54(10)
C(8)-C(7)-B(1)	129.76(11)
C(6)-C(7)-B(1)	125.44(11)
C(7)-C(8)-O(1)	112.61(10)
C(7)-C(8)-C(9)	135.72(11)
O(1)-C(8)-C(9)	111.65(10)
C(14)-C(9)-C(10)	119.11(11)
C(14)-C(9)-C(8)	121.36(11)
C(10)-C(9)-C(8)	119.35(11)
C(11)-C(10)-C(9)	120.31(12)
C(10)-C(11)-C(12)	120.04(13)

C(13)-C(12)-C(11)	120.00(12)
C(12)-C(13)-C(14)	120.32(12)
C(13)-C(14)-C(9)	120.21(12)
O(3)-C(15)-O(2)	124.09(12)
O(3)-C(15)-C(16)	124.38(11)
O(2)-C(15)-C(16)	111.50(10)
N(1)-C(16)-C(15)	107.05(9)
O(5)-C(17)-O(4)	124.38(12)
O(5)-C(17)-C(18)	124.25(12)
O(4)-C(17)-C(18)	111.37(10)
N(1)-C(18)-C(17)	107.21(10)
O(6)-C(20)-C(21)#1	120.77(14)
O(6)-C(20)-C(21)	120.77(14)
C(21)#1-C(20)-C(21)	118.5(3)

Symmetry transformations used to generate equivalent atoms:

#1 –x,y,-z+1/2

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4b**. 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}
B(1)	14(1)	12(1)	14(1)	1(1)	0(1)	4(1)
N(1)	14(1)	11(1)	14(1)	-1(1)	0(1)	2(1)
O(1)	17(1)	18(1)	12(1)	0(1)	2(1)	-3(1)
O(2)	14(1)	22(1)	13(1)	4(1)	1(1)	3(1)
O(3)	19(1)	24(1)	16(1)	1(1)	3(1)	-3(1)
O(4)	24(1)	12(1)	15(1)	-1(1)	0(1)	4(1)
O(5)	31(1)	14(1)	30(1)	-4(1)	0(1)	-3(1)
C(1)	14(1)	14(1)	16(1)	2(1)	0(1)	1(1)
C(2)	21(1)	20(1)	14(1)	1(1)	2(1)	0(1)
C(3)	22(1)	23(1)	18(1)	4(1)	5(1)	-2(1)
C(4)	20(1)	21(1)	23(1)	1(1)	3(1)	-5(1)
C(5)	19(1)	18(1)	17(1)	-1(1)	1(1)	-1(1)
C(6)	15(1)	13(1)	15(1)	1(1)	2(1)	3(1)
C(7)	14(1)	12(1)	14(1)	2(1)	1(1)	2(1)
C(8)	15(1)	14(1)	12(1)	1(1)	2(1)	3(1)
C(9)	15(1)	13(1)	15(1)	-2(1)	3(1)	0(1)
C(10)	18(1)	17(1)	15(1)	-1(1)	2(1)	1(1)
C(11)	17(1)	22(1)	18(1)	-5(1)	2(1)	-1(1)
C(12)	20(1)	16(1)	22(1)	-5(1)	7(1)	-3(1)
C(13)	23(1)	13(1)	21(1)	0(1)	7(1)	1(1)
C(14)	18(1)	16(1)	16(1)	-1(1)	2(1)	2(1)
C(15)	17(1)	12(1)	13(1)	-2(1)	0(1)	0(1)
C(16)	18(1)	17(1)	15(1)	4(1)	2(1)	3(1)
C(17)	19(1)	15(1)	18(1)	-1(1)	4(1)	1(1)
C(18)	21(1)	14(1)	34(1)	-5(1)	-11(1)	1(1)
C(19)	17(1)	20(1)	17(1)	-2(1)	2(1)	8(1)
O(6)	46(1)	15(1)	28(1)	0	0(1)	0
C(20)	34(1)	17(1)	21(1)	0	12(1)	0
C(21)	88(2)	75(2)	48(1)	-36(1)	33(1)	-60(1)

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

	x	y	z	U(eq)
H(21A)	2079	3610	2583	106
H(21B)	2485	2742	2818	106
H(21C)	719	3411	2929	106
H(2)	2570(20)	1147(10)	-66(4)	21(4)
H(3)	5310(30)	2126(11)	-4(4)	24(4)
H(4)	6320(30)	2658(11)	570(5)	30(4)
H(5)	4530(20)	2206(10)	1094(4)	18(4)
H(10)	-3570(20)	302(10)	499(4)	15(4)
H(11)	-6090(30)	-793(11)	551(5)	26(4)
H(12)	-5750(30)	-1916(12)	986(4)	28(4)
H(13)	-3000(20)	-1963(10)	1386(4)	20(4)
H(14)	-370(20)	-885(10)	1332(4)	22(4)
H(16A)	1590(20)	262(11)	2260(4)	24(4)
H(16B)	1300(30)	-483(12)	1969(5)	32(5)
H(18A)	3530(30)	1356(13)	2206(5)	42(5)
H(18B)	5100(30)	1319(13)	1872(5)	44(5)
H(19A)	3050(30)	-411(11)	1437(4)	28(4)
H(19B)	4770(30)	-253(11)	1742(4)	23(4)
H(19C)	4690(30)	362(11)	1390(5)	28(4)