SPIROBORATES REVISITED. X-RAY CRYSTAL AND MOLECULAR STRUCTURES OF BORON CHELATE COMPOUNDS WITH TROPOLONE AND 1,3-DIKETONES

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ABSTRACT

The crystal and molecular structures of boron chelates (spiroborates **1a**, **1b** and **3**) and **2b** were determined. Together with the structures of chelates **2a** and **4** which had been published earlier by Rettig and Trotter, these data allow a general discussion of bond distances and angles in boron chelates with 5- and 6-membered chelate rings possessing electronic delocalization due to pairs of fully equivalent oxygens connected to the sp^3-hybridized boron atom. A linear correlation is apparent between the "tetrahedral character" and the ^{11}B-NMR chemical shifts.

INTRODUCTION

Neutral chelates can be obtained from boric or borinic esters (2-alkoxy-1,3,2-benzodioxaboroles, or diarylborinic esters) in their reaction with 1,3-diketones or tropolones.[1] Thus were prepared chelates with six-membered chelate rings (with 1,3-diketones, e. g. **1, 2**) and with five-membered chelate rings (with tropolones, e. g. **3, 4**). Such chelates have high dipole moments.[2] Complete electronic delocalization in the moiety bearing the positive charge (as shown by the ^{13}C-NMR spectrum) leads to equivalence of the two oxygen heteroatoms of the chelate ring, contributing to the stability of the chelate. This assertion is borne out by the higher stability towards hydrolysis of such chelates having sp^3-hybridized boron atoms than the corresponding starting materials (boric or borinic esters) with sp^2-hybridized boron atoms; also, no stable chelates were obtained in cases when nonequivalent oxygen atoms would result : the reaction of the same boric or borinic esters with 3-hydroxyketones, 3-hydroxy-2-pyrones or 3-hydroxy-4-pyrones affords no crystalline chelates.

An X-ray study of the chelate with arsenic instead of boron,[3] whose NMR spectra indicated a similar equivalence of atoms in the chelate ring, even at the lowest temperatures attainable, revealed an interesting difference in As—O bond lengths, indicative of rapid degenerate rearrangement (fluctuating structure).[4] Since in the above case the arsenic atom has an extra unshared electron pair, a chelate ring would have led to a trigonal-bipyramidal structure around the arsenic atom. One could conceive that boron chelates could also be fluctuating molecules with sp^2-hybridized boron atoms. X-Ray diffraction can diagnose with certainty the real molecular structure.

Table 1: Crystallographic data and instrumental setting for compounds **1a**, **1b**, **2b** and **3**.

compound	**1a**[a]	**1b**[a]	**2b**[a]	**3**[a]
formula	$C_{11}H_{11}BO_4$	$C_{21}H_{15}BO_4$	$C_{27}H_{21}BO_2$	$C_{13}H_9BO_4$
fw	218.0	342.8	388.3	240.0
Crystal dimensions	0.4x0.4x0.6	0.2x0.2x0.4	0.25x0.25x0.4	0.4x0.4x0.5
space group	P $2_1/n$	C 2/c	P -1	P 2_1
a (Å)	10.054 (1)	17.414(2)	8.125(1)	6.225(1)
b (Å)	8.505 (1)	11.529(1)	12.269(1)	8.529(1)
c (Å)	12.603 (1)	9.850(1)	21.744(2)	10.571(1)
α (°)			76.921(5)	
β (°)	95.39 (1)	121.83(1)	81.109(5)	98.73(1)
γ (°)			80.344(4)	
V (Å^3)	1072.8 (1)	1680.2(3)	2065.9.2)	554.9(1)
Z	4	4	4	2
F(000)	456	704	816	248
linear abs coeff mm^{-1}	0.094	0.086	0.071	0.098
ρ (calc) g cm^{-3}	1.35	1.35	1.25	1.43
scan width (°)	0.52 + 0.47 tg θ	0.44 + 0.46 tg θ	0.76 + 0.65 tg θ	0.51 + 0.51 tg θ
no of data collected	2905	2238	9421	1491
no of unique data collected	2583	2024	8991	1416
No of reflections with I > 3 σ I	1960	1293	3288	1259
R(int)	0.018	0.026	0.012	0.025
abs. coeff. corr.	0.75 < coeff < 1.26	0.77 < coeff < 1.38	0.88 < coeff < 1.04	0.78 < coeff < 1.25
R	0.045	0.042	0.046	0.038
Rw	0.042	0.036	0.050	0.033
no. of variables	180	143	512	165

a) Radiation MoKα (λ =.71069 Å) , Diffractometer CAD4-Enraf-Nonius, scan type ω/2θ, θ limits (°) 2- 28.

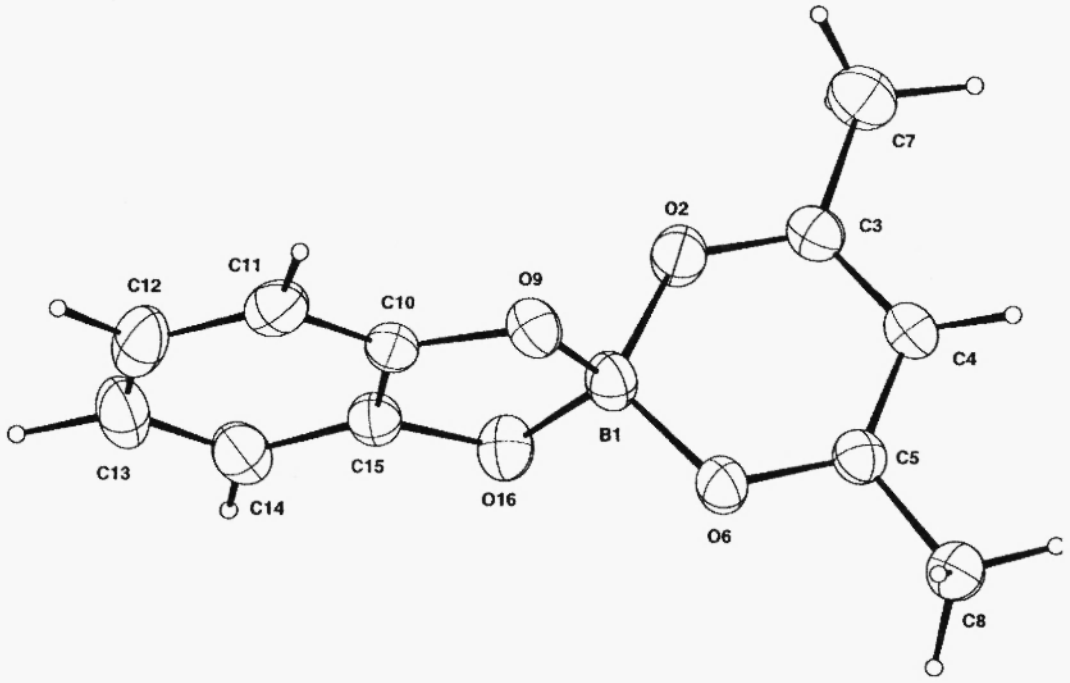

Fig. 1A. Structure and numbering of compound **1a**

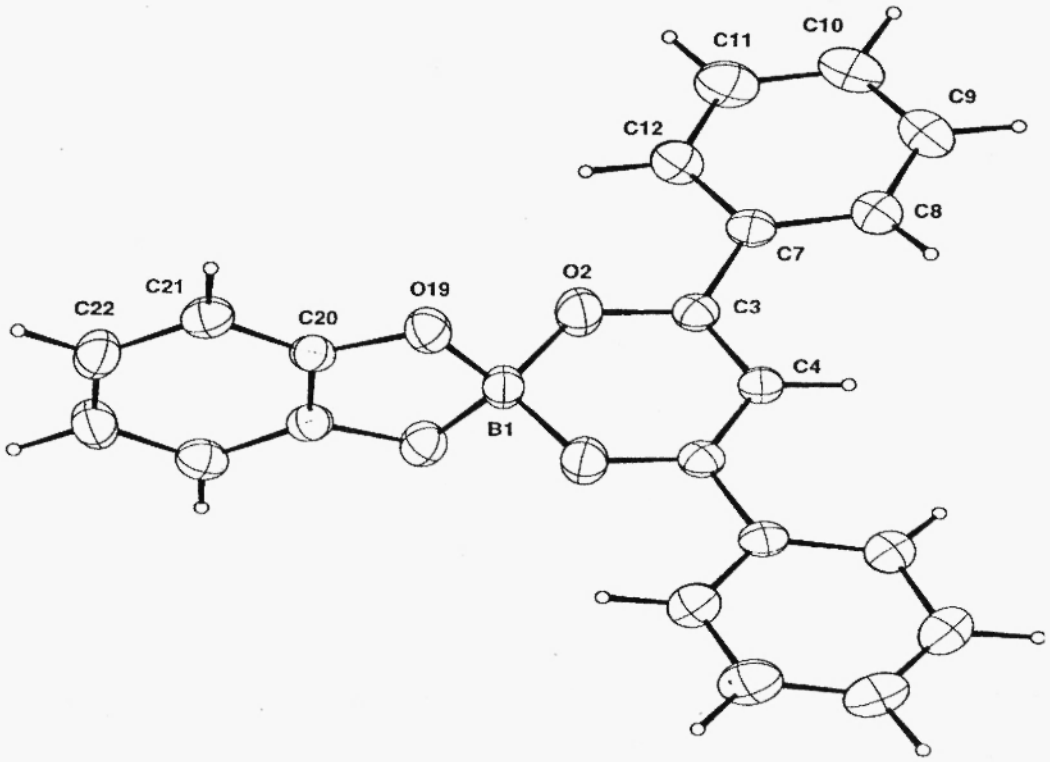

Fig. 1B. Structure and numbering of compound **1b**:
because of symmetry, only half of the molecule is numbered

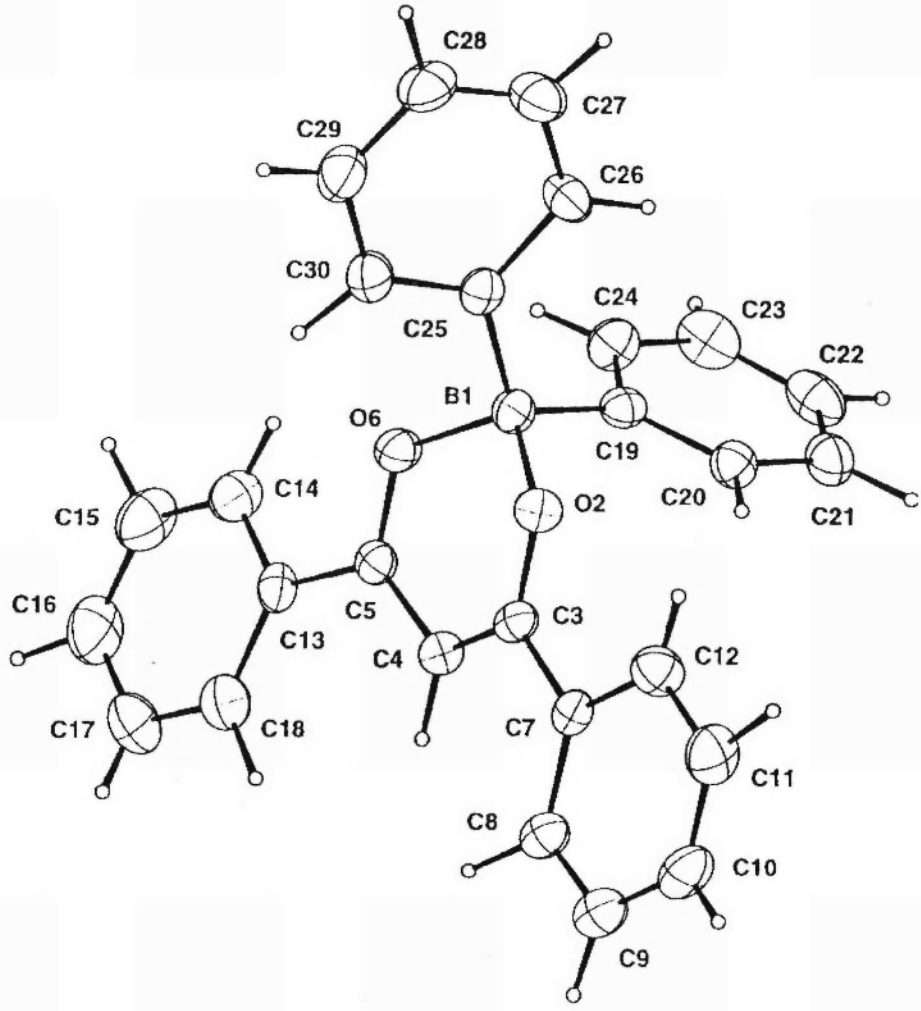

Fig. 1C. Structure and numbering of compound **2b**

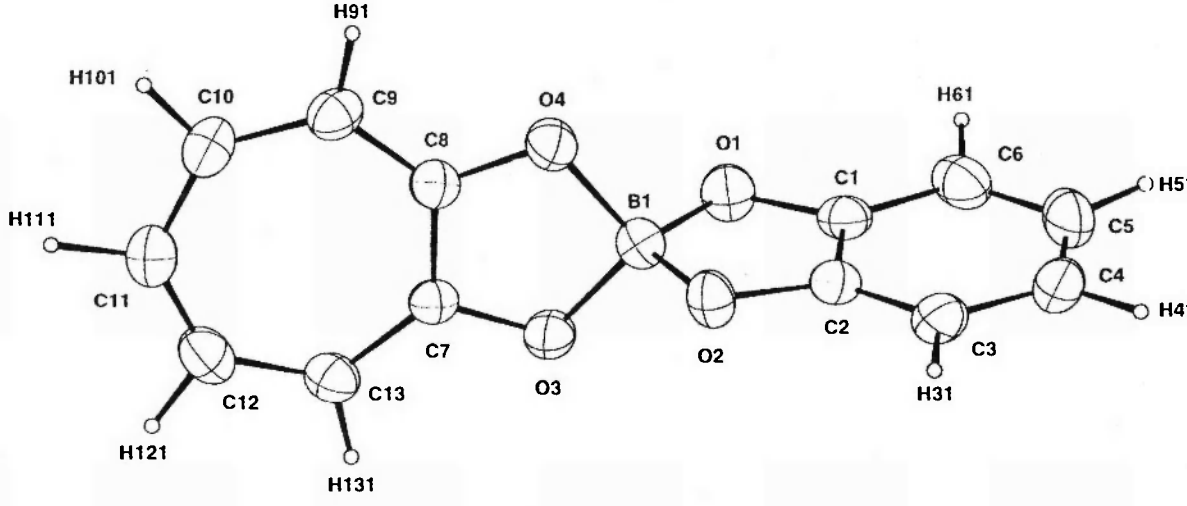

Fig. 1D. Structure and numbering of compound **3**

Table 2: Fractional atomic coordinates for compounds **1a**, **1b**, **2b** and **3**.

Compound **1a**

Atom	x/a	y/b	z/c	U(equiv)
B(1)	0.3861(2)	0.1159(3)	0.7135(2)	0.0445
O(2)	0.3925(1)	-0.0197(2)	0.6378(1)	0.0512
O(6)	0.2470(1)	0.1722(2)	0.7118(1)	0.0479
O(9)	0.4361(1)	0.0657(2)	0.8205(1)	0.0456
O(16)	0.4742(1)	0.2393(2)	0.6824(1)	0.0482
C(3)	0.2879(2)	-0.0906(2)	0.5944(1)	0.0419
C(4)	0.1618(2)	-0.0385(2)	0.6086(2)	0.0427
C(5)	0.1456(2)	0.0959(2)	0.6663(2)	0.0398
C(7)	0.3144(3)	-0.2292(3)	0.5272(2)	0.0584
C(8)	0.0136(2)	0.1662(3)	0.6798(2)	0.0545
C(10)	0.5550(2)	0.1425(2)	0.8431(2)	0.0386
C(11)	0.6433(2)	0.1286(3)	0.9325(2)	0.0496
C(12)	0.7580(2)	0.2215(4)	0.9366(2)	0.0562
C(13)	0.7802(2)	0.3238(3)	0.8557(2)	0.0566
C(14)	0.6894(2)	0.3383(3)	0.7654(2)	0.0507
C(15)	0.5774(2)	0.2461(2)	0.7613(2)	0.0401

Compound **1b**

Atom	x/a	y/b	z/c	U(equiv)
B(1)	0.0000	0.2267(3)	0.2500	0.0495
O(2)	0.0597(1)	0.3013(1)	0.2205(2)	0.0555
O(19)	-0.0540(1)	0.1520(1)	0.1132(2)	0.0503
C(3)	0.0581(1)	0.4133(2)	0.2199(2)	0.0385
C(4)	0.0000	0.4730(3)	0.2500	0.0411
C(7)	0.1217(1)	0.4693(2)	0.1847(2)	0.0392
C(8)	0.1233(2)	0.5886(2)	0.1677(3)	0.0476
C(9)	0.1832(2)	0.6385(2)	0.1330(3)	0.0525
C(10)	0.2427(2)	0.5699(3)	0.1167(3)	0.0569
C(11)	0.2417(2)	0.4519(3)	0.1330(3)	0.0629
C(12)	0.1813(2)	0.4009(2)	0.1658(3)	0.0512
C(20)	-0.0314(1)	0.0408(2)	0.1681(2)	0.0399
C(21)	-0.0628(2)	-0.0603(2)	0.0852(3)	0.0484
C(22)	-0.0305(2)	-0.1632(2)	0.1687(3)	0.0557

Compound **2b**

Atom	x/a	y/b	z/c	U(equiv)
B(1)	0.7772(7)	0.7323(4)	0.0879(2)	0.0391
B(51)	0.8344(7)	0.2905(4)	0.4104(2)	0.0405
O(2)	0.6862(4)	0.6357(2)	0.0817(1)	0.0413
O(6)	0.8385(4)	0.7893(2)	0.0195(1)	0.0434
O(52)	0.8551(4)	0.3019(2)	0.4775(1)	0.0435
O(56)	0.7438(4)	0.1893(2)	0.4176(1)	0.0432
C(3)	0.7416(5)	0.5784(3)	0.0379(2)	0.0351
C(4)	0.8527(5)	0.6191(4)	-0.0140(2)	0.0387
C(5)	0.8866(5)	0.7299(4)	-0.0237(2)	0.0360
C(7)	0.6748(5)	0.4707(3)	0.0468(2)	0.0347
C(8)	0.7047(6)	0.4062(4)	-0.0002(2)	0.0439
C(9)	0.6394(6)	0.3062(4)	0.0104(3)	0.0535
C(10)	0.5469(7)	0.2684(4)	0.0682(3)	0.0565
C(11)	0.5151(7)	0.3309(5)	0.1141(3)	0.0589
C(12)	0.5796(6)	0.4317(4)	0.1045(2)	0.0515
C(13)	0.9768(6)	0.7879(4)	-0.0832(2)	0.0399
C(14)	1.0391(6)	0.8871(4)	-0.0842(2)	0.0518
C(15)	1.1283(8)	0.9404(5)	-0.1388(3)	0.0684
C(16)	1.1515(8)	0.8990(6)	-0.1926(3)	0.0716
C(17)	1.0914(9)	0.8018(6)	-0.1928(3)	0.0720
C(18)	1.0024(7)	0.7458(5)	-0.1382(3)	0.0604

C(19)	0.9362(5)	0.6789(4)	0.1251(2)	0.0385
C(20)	0.9587(6)	0.5674(4)	0.1588(2)	0.0447
C(21)	1.0976(7)	0.5224(4)	0.1916(2)	0.0540
C(22)	1.2181(6)	0.5883(5)	0.1906(2)	0.0569
C(23)	1.2010(6)	0.6989(5)	0.1582(3)	0.0588
C(24)	1.0621(6)	0.7434(4)	0.1259(2)	0.0513
C(25)	0.6373(5)	0.8218(4)	0.1166(2)	0.0380
C(26)	0.6120(6)	0.8260(4)	0.1812(2)	0.0472
C(27)	0.4824(7)	0.9020(5)	0.2048(2)	0.0598
C(28)	0.3776(7)	0.9724(5)	0.1661(3)	0.0595
C(29)	0.4002(7)	0.9708(4)	0.1028(3)	0.0581
C(30)	0.5278(6)	0.8954(4)	0.0786(2)	0.0494
C(53)	0.8727(5)	0.2129(4)	0.5225(2)	0.0367
C(54)	0.8429(6)	0.1088(4)	0.5159(2)	0.0389
C(55)	0.7685(5)	0.1013(4)	0.4634(2)	0.0355
C(57)	0.9216(5)	0.2331(4)	0.5811(2)	0.0396
C(58)	0.8972(7)	0.1577(4)	0.6394(2)	0.0530
C(59)	0.9467(8)	0.1788(5)	0.6935(2)	0.0628
C(60)	1.0199(7)	0.2712(6)	0.6899(3)	0.0594
C(61)	1.0460(7)	0.3466(5)	0.6333(3)	0.0593
C(62)	0.9962(6)	0.3270(4)	0.5789(2)	0.0507
C(63)	0.7083(5)	-0.0005(4)	0.4562(2)	0.0369
C(64)	0.6585(7)	-0.0026(4)	0.3981(2)	0.0507
C(65)	0.6018(7)	-0.0977(5)	0.3903(3)	0.0627
C(66)	0.5946(7)	-0.1910(4)	0.4389(3)	0.0586
C(67)	0.6434(6)	-0.1902(4)	0.4959(3)	0.0511
C(68)	0.7017(6)	-0.0961(4)	0.5050(2)	0.0439
C(69)	1.0188(6)	0.2672(4)	0.3723(2)	0.0414
C(70)	1.1387(6)	0.3376(4)	0.3669(3)	0.0553
C(71)	1.2981(7)	0.3207(5)	0.3347(3)	0.0625
C(72)	1.3404(7)	0.2283(6)	0.3055(3)	0.0663
C(73)	1.2258(8)	0.1569(5)	0.3089(3)	0.0688
C(74)	1.0667(7)	0.1758(4)	0.3414(2)	0.0549
C(75)	0.7128(6)	0.4000(4)	0.3806(2)	0.0401
C(76)	0.5818(6)	0.4511(4)	0.4184(2)	0.0493
C(77)	0.4705(7)	0.5430(5)	0.3933(3)	0.0588
C(78)	0.4867(7)	0.5876(4)	0.3291(3)	0.0588
C(79)	0.6155(7)	0.5382(4)	0.2906(2)	0.0563
C(80)	0.7255(6)	0.4478(4)	0.3158(2)	0.0478

Compound **3**

Atom	x/a	y/b	z/c	U(equiv)
O(1)	-0.1696(3)	0.7587(2)	0.6995(2)	0.0528
O(2)	0.1080(3)	0.5750(3)	0.7489(2)	0.0511
O(3)	0.1932(3)	0.8167(3)	0.6452(2)	0.0494
O(4)	-0.0219(3)	0.6341(3)	0.5234(2)	0.0529
B(1)	0.0228(5)	0.6958(4)	0.6585(3)	0.0471
C(1)	-0.1967(4)	0.6761(4)	0.8072(3)	0.0461
C(2)	-0.0301(4)	0.5691(4)	0.8384(3)	0.0469
C(3)	-0.3634(5)	0.6863(5)	0.8788(3)	0.0592
C(4)	-0.3529(6)	0.5869(5)	0.9840(3)	0.0674
C(5)	-0.1845(6)	0.4849(5)	1.0165(3)	0.0675
C(6)	-0.0171(5)	0.4732(4)	0.9423(3)	0.0591
C(7)	0.2521(4)	0.8050(3)	0.5307(2)	0.0408
C(8)	0.1179(4)	0.6944(3)	0.4556(3)	0.0435
C(9)	0.1204(5)	0.6504(4)	0.3305(3)	0.0529
C(10)	0.2645(6)	0.6988(4)	0.2504(3)	0.0580
C(11)	0.4389(5)	0.7997(4)	0.2755(3)	0.0596
C(12)	0.5060(5)	0.8850(4)	0.3835(3)	0.0596
C(13)	0.4256(5)	0.8892(4)	0.4985(3)	0.0532