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The Colour of Chelates of Boron. An *X*-Ray Structural Investigation of Bis(4-methylphenyl)boryl and 9-Borabicyclo-[3.3.1]nonyl Acetylacetonates

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The molecular structures of the colourless bis(4-methylphenyl)boryl and the orange coloured 9-borabicyclo[3.3.1]non-9-yl acetylacetonates (**4** and **5**, respectively) have been determined by *X*-ray analysis. The C – O bond lengths in **4** are significantly (about 0.029 Å) longer than in **5**. It is suggested that variation of the π bond order in the C – O bonds is responsible for the shifts in the electronic spectra observed for the various chelates of 1,3-diketones and related compounds.

Die Farbe von Bor-Chelaten. Röntgenstruktur-Untersuchung von Bis(4-methylphenyl)boryl- und 9-Borabicyclo[3.3.1]nonyl-acetylacetonaten

Die Molekülstrukturen des farblosen Bis(4-methylphenyl)boryl- und des orangefarbenen 9-Borabicyclo[3.3.1]non-9-yl-acetylacetonats (**4** und **5**) wurden durch Röntgenstrukturanalyse ermittelt. Die C – O-Abstände in **4** sind merklich (ca. 0.029 Å) länger als die in **5**. Es wird vermutet, daß der unterschiedliche π-Charakter in den C – O-Bindungen die Verschiebungen im Elektronenspektrum der verschiedenen Chelate von 1,3-Diketonen und verwandten Verbindungen verursacht.

In the course of our investigations on the mechanism of thermochromism in the boron heterocycles **1** we had observed that the aryl, in contrast to the alkyl, derivatives remained colourless even when cooled to very low temperatures[1,2]. Structural investigations had shown that the (colourless-yellow[3]) reversible solid state reactions of the alkyl derivatives were due to chelate bond formation between the boron atoms of one molecule of **1** with the carbonyl oxygens of the neighbouring molecules. The failure of this reaction in the case of the aryl derivatives was explained by the decrease of the Lewis acidity of the boron due to p-orbital overlap from the substituent aryl groups. This would thus decrease the chelating tendency of the boron atoms and therefore cause the absence of the yellow coloured low temperature forms observed for the alkyl-substituted **1**. Many boron compounds including the acetylacetonates **2** form coloured chelates (yellow-orange)[4] when the substituents on the boron atoms are alkyl[5] and give colourless chelates with diaryl-[5], difluoro-[6,7], or diacetyl-[8] substituents.

A closer inspection of the chelate **2** for substituents R = aryl readily reveals that any electronic overlap from the aromatic substituents to the boron atom would rupture the chelate bonding and lead to **3a** or **b**.

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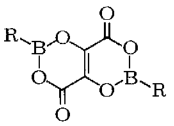

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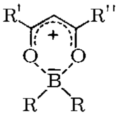

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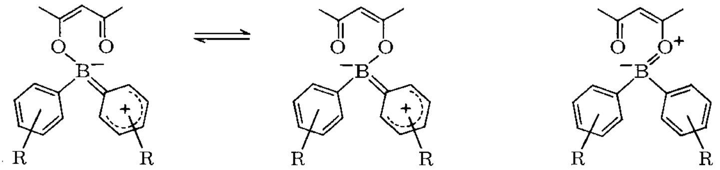


3a **3b**

The observation of only a broad chelate band at 1545 cm^{-1} in the infra-red spectrum of the aryl derivatives[2], the absence of a free carbonyl band as well as a non-variant ^{13}C NMR spectrum of bis(4-methylphenyl)boryl acetylacetonate (**4**) at 50.3 MHz down to a temperature of −100 °C[9] are in conformity with the symmetrical structure **2** and rule out any significant contribution of structures **3a** and **b**. It seemed to us that a crystallographic analysis and comparison of a dialkyl- and a diarylboryl acetylacetonate would reveal some feature which would lead to the clarification of the differences of their respective electronic spectra.

Results and Discussion

The *X*-ray analysis of bis(4-methylphenyl)boryl and 9-borabicyclo[3.3.1]non-9-yl acetylacetonate (**4** and **5**, respectively) confirmed the chelate structure **2** in the solid state. The structures are shown in Fig. 1 with their respective crystallographic numbering schemes. The appropriate bond distances and angles are shown in Table 1 and compared with those reported for diphenylboryl acetylacetonate (**6**)[10], (benzoylacetonato)difluoroborate (**7**)[6] and bis(acetato)(acetylacetonato)borate (**8**)[8].

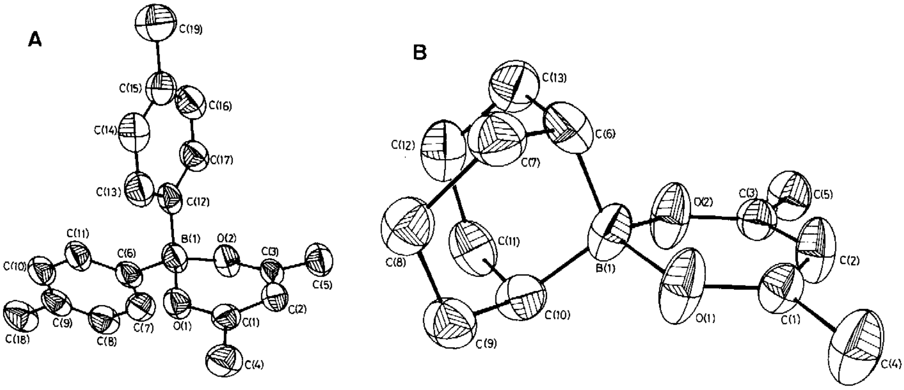
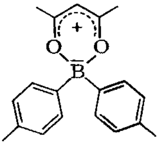


Fig. 1. Perspective Views of Molecules of **4** (A) and **5** (B) Showing the Atom Numbering Scheme

Table 1. Selected Bond Lengths (Å) and Angles (°) for Compounds **4**–**8**

	4	5	6[10a]	7[6]	8[8]
B(1) – O(1)	1.552(5)	1.550(5)	1.530	1.483	1.473
B(1) – O(2)	1.530(5)	1.558(5)	1.535	1.490	1.469
B(1) – C(6)	1.628(6)	1.588(4)	1.599	–	–
B(1) – C(x)	1.630(6)	1.571(5)	1.600	–	–
O(1) – C(1)	1.293(5)	1.270(4)	1.292	1.304	1.293
O(2) – C(3)	1.305(5)	1.270(4)	1.290	1.306	1.298
C(1) – C(2)	1.371(5)	1.363(6)	1.375	1.390	1.359
C(1) – C(4)	1.483(5)	1.489(5)	1.376	–	–
C(2) – C(3)	1.364(5)	1.353(5)	1.487	1.389	1.365
C(3) – C(5)	1.484(5)	1.496(5)	1.485	–	–
C(6) – B(1) – C(x)	118.1(3)	108.6(3)	115.13	–	–
O(1) – B(1) – O(2)	106.2(3)	106.1(3)	107.1	111.4	112.2
O(1) – B(1) – C(6)	106.6(3)	110.9(3)	109.15	–	–
O(1) – B(1) – C(x)	108.9(3)	110.4(3)	108.35	–	–
O(2) – B(1) – C(6)	107.8(3)	109.7(3)	108.71	–	–
O(2) – B(1) – C(x)	108.7(3)	111.1(3)	108.14	–	–
B(1) – O(1) – C(1)	120.0(3)	123.7(3)	119.48	123.4	122.4
B(1) – O(2) – C(3)	119.1(3)	123.4(3)	119.38	122.6	121.8
O(1) – C(1) – C(2)	120.9(3)	121.0(3)	121.26	122.0	121.9
O(2) – C(3) – C(2)	121.3(3)	121.2(3)	115.5	121.2	–
C(1) – C(2) – C(3)	121.0(4)	122.4(3)	120.39	119.4	120.1

[a] Values listed are averages of those reported for the mono- and triclinic forms of **6**[10].



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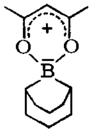

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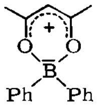

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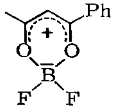

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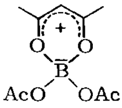

8

It can be seen that the bond lengths and angles in the six-membered chelate ring of **4** are comparable to those found for **6**[10]. This ring is, due to the unequal B–O bond lengths, slightly distorted. However, on average these bonds are somewhat (by about 0.01 Å) shorter than those found in **5**. The C–O1 and C–O2 bonds in **4** are by about 0.029 Å (av.) longer than in **5** and are of the same magnitude as found in **7** and **8**. With the exception of the O1–B–O2 angles [106.1° (av.) in **4** and **5** compared with 111.8° (av.) for **7** and **8**] the other bonds and angles within the chelate rings of **4** and **5** show only slight variations and are similar to those found for the difluoro and diacetyl derivatives **7** and **8**. As expected the exocyclic C–B–C angle for the 9-BBN derivative **5** with 108.6° is smaller than the 118° found between the substituent aryl groups in **4**. The latter angle is also larger than that found in **7**[6] and **8**[8] and in other diarylboryl chelates[11]. Furthermore, the planes of the aryl groups in **4** are twisted with respect to each other with an angle of 74.0°. This arrangement of the aryl groups is not unusual and is similarly found in other diarylboryl chelates[11]. The chelate rings in **4** and **5** are bent around O1 and O2. In **4** the two planes described by the mean plane of O1–C1–C2–C3–O2 and O1–B–O2 are bent at an angle of about 31.7° while in **5** this angle is 13.7°. This extra bending of the C_3BO_2 ring in the colourless **4**, or more generally its conformation cannot be considered to cause the observed shifts of the electronic spectra, as the likewise colourless difluoro (**7**) and diacetyl (**8**) derivatives have been found to be planar[6,8].

A common structural feature in the colourless chelates **4** and **6**–**9** which is significantly different from that of the coloured **5** is the larger C–O bond lengths observed.

This elongation of the bond lengths is considered to be the result of the action of the electron withdrawing substituents Ar, F, or OAc and indicates a reduction of the π bond order in these bonds. This will lead to a larger separation of the negative charge centered on the boron atom from the positive charge which thus becomes distributed mainly on the three carbon atoms of the C_3BO_2 ring. It is therefore suggested that the shifting of the electronic spectra is a substituent effect which changes the degree of the interaction between the charge on the boron atom and the electron cloud distributed over the rest of the chelate ring.

This interpretation is supported by the effect the substituents have on the position of the long wave length chelate band (186 – 347 nm) of all the so far published spectral results. Thus the data for four substituents have been linearly correlated with the Taft σ^* values12) and it appears from other published data5,12,13) that this correlation can be extended to cover other substituents.

In addition to the effect of the substituents from the boron side of the chelate ring, it can also be expected that substitution of groups with a negative I effect on the acetylacetone moiety should lead to an increase of the π bond order and lead to a red shift of the spectrum. This is substantiated in the spectra of the chelate of the related enamino ketones14) and the reported colours of the acylamidine boryl chelates15).

M. Y. is grateful to the *Max-Planck-Institut für Kohlenforschung* for a fellowship.

Experimental Part

Table 2. Atom Coordinates and Temperature Factors (Å^2) for **4**

Atom	x	y	z	U
B(1)	0.7019(5)	-0.1323(4)	0.3728(3)	0.070(2)*
O(1)	0.7971(2)	-0.0727(2)	0.4565(2)	0.072(1)*
O(2)	0.6090(3)	-0.0530(2)	0.3099(2)	0.076(1)*
C(1)	0.7473(4)	0.0077(3)	0.4902(3)	0.060(1)*
C(2)	0.6238(4)	0.0533(3)	0.4418(3)	0.063(1)*
C(3)	0.5617(4)	0.0250(3)	0.3506(3)	0.060(2)*
C(4)	0.8381(4)	0.0478(3)	0.5800(3)	0.081(2)*
C(5)	0.4428(4)	0.0812(4)	0.2878(3)	0.087(2)*
C(7)	0.8549(3)	-0.1241(2)	0.2401(2)	0.080(2)*
C(8)	0.9509(3)	-0.1655(2)	0.1889(2)	0.089(2)*
C(9)	1.0024(3)	-0.2641(2)	0.2085(2)	0.081(2)*
C(10)	0.9580(3)	-0.3213(2)	0.2792(2)	0.084(2)*
C(11)	0.8620(3)	-0.2800(2)	0.3303(2)	0.075(2)*
C(6)	0.8104(3)	-0.1814(2)	0.3108(2)	0.069(2)*
C(13)	0.6440(2)	-0.2549(2)	0.5053(2)	0.080(2)*
C(14)	0.5536(2)	-0.3213(2)	0.5408(2)	0.090(2)*
C(15)	0.4161(2)	-0.3417(2)	0.4872(2)	0.088(2)*
C(16)	0.3691(2)	-0.2956(2)	0.3982(2)	0.085(2)*
C(17)	0.4595(2)	-0.2291(2)	0.3627(2)	0.076(2)*
C(12)	0.5970(2)	-0.2088(2)	0.4163(2)	0.065(2)*
C(18)	1.1058(5)	-0.3089(4)	0.1504(4)	0.113(2)*
C(19)	0.3157(6)	-0.4156(4)	0.5265(5)	0.131(3)*

*) Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 3. Atom Coordinates and Temperature Factors (Å^2) for **5**

Atom	x	y	z	U
C(1)	0.2167(4)	0.4180(3)	0.3646(3)	0.051(1)*
C(2)	0.3527(5)	0.3670(4)	0.3174(4)	0.070(2)*
C(3)	0.4111(4)	0.4344(3)	0.2213(3)	0.048(1)*
C(4)	0.1336(5)	0.3350(4)	0.4582(4)	0.078(2)*
C(5)	0.5433(5)	0.3712(4)	0.1568(3)	0.067(2)*
C(6)	0.3549(4)	0.7985(4)	0.3219(3)	0.061(1)*
C(7)	0.2326(5)	0.8835(4)	0.3878(3)	0.063(2)*
C(8)	0.0385(4)	0.9110(3)	0.2909(3)	0.060(1)*
C(9)	-0.0750(4)	0.7754(4)	0.1879(3)	0.060(1)*
C(10)	0.0472(4)	0.6911(3)	0.1219(3)	0.059(2)*
C(11)	0.1297(5)	0.7849(4)	0.0287(3)	0.071(2)*
C(12)	0.2867(5)	0.9229(4)	0.0996(4)	0.076(2)*
C(13)	0.4384(5)	0.8938(4)	0.2293(4)	0.072(2)*
O(1)	0.1480(4)	0.5385(2)	0.3265(3)	0.081(1)*
O(2)	0.3482(3)	0.5541(2)	0.1751(2)	0.079(1)*
B(1)	0.2233(6)	0.6460(4)	0.2359(4)	0.060(2)*

*) Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

X-ray measurements and calculations[16]: Syntex R3 four cycle diffractometer with a Nova 3/12 (Data General), Nicolet P3 and SHELXTL software[17]. Structure solutions were carried out by direct method and all hydrogen atoms were included.

For compound **4**[5], $C_{19}H_{21}BO_2$, monoclinic, S.G. $P2_1/c$; $a = 9.515(2)$, $b = 13.164(5)$, $c = 14.281(4)$ Å, $\beta = 102.16(2)°$, $V = 1748.8(9)$ Å^3, $D_x = 1.11$ g/cm^3, $\lambda = 0.71069$ Å, 1335 unique reflexions were observed $[F_o \geqslant 3.5\ \sigma(F_o)]$. $R = 0.054$, $R_w = 0.061$ $[w^{-1} = \sigma^2(F_o) + 0.00095 \cdot F_o^2]$, maximum rest electron density 0.18 e/Å^3.

For compound **5**[5], $C_{13}H_{21}BO_2$, triclinic, S.G. $P\bar{1}$; $a = 7.327(2)$, $b = 8.833(2)$, $c = 10.524(3)$ Å, $\alpha = 93.09(2)°$, $\beta = 108.61(2)°$, $\gamma = 97.89(2)°$, $V = 635.9(3)$ Å^3, $Z = 2$, $D_x = 1.14$ g/cm^3, $\lambda = 0.71069$ Å, 1096 unique reflexions were observed $[F_o \geqslant 3.5\ \sigma(F_o)]$. $R = 0.052$, $R_w = 0.052$ $[w^{-1} = \sigma^2(F_o) + 0.0041 \cdot F_o^2]$, maximum rest electron density 0.16 e/Å^3.

The atom coordinates and temperature factors for compounds **4** and **5** are shown in Tables 2 and 3, respectively.

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[3] The solid state electronic spectrum of **1** (R = Et or *n*-Pr) shows that the enedione band at 280 nm of the colourless form is transformed on cooling to a chelate band at 400 nm in the yellow form of the crystals (*M. Yalpani,* unpublished results).

[4] In the electronic spectra of the dialkylboryl acetylacetonates the longer wavelength chelate absorption band extends into the visible region (up to 476 nm for **5**). For the diarylboryl acetylacetonates this band ends at 384 nm. This end absorption is thus responsible for the colour of some of the chelates (cf. data in Table 1, of ref.[5]).

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16) Further details and basic data concerning the *X*-ray analysis may be obtained from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen (W. Germany) by specifying registry number CSD 50858, author, and the reference to this publication.

17) *G. M. Sheldrick,* SHELXTL (1981). An integrated system for solving, refining, and displaying crystal structures from diffraction data. University of Göttingen.

[36/84]