Synthesis and X-ray study of a bis-diphenylboron chelate of 3-(diaminomethylene)pentane-2,4-dione

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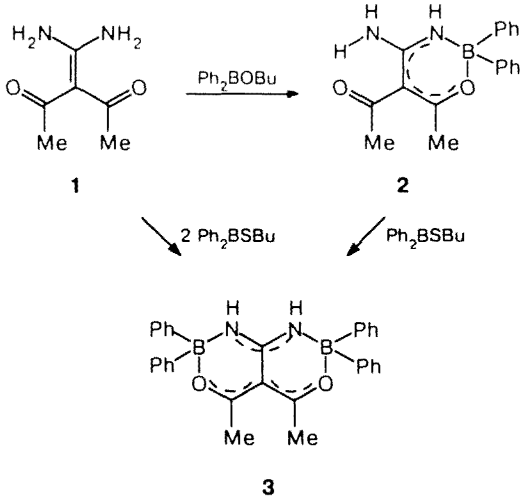
A bis-diphenylboron chelate has been synthesized from 3-(diaminomethylene)pentane-2,4-dione through the action of (butylthio)diphenylborane and its molecular and crystal structures have been determined. The two boron-containing rings have the same six-membered skeleton but differ substantially in conformation and geometric parameters.

Key words: 3-(diaminomethylene)pentane-2,4-dione, (butylthio)diphenylborane, diphenylboron chelates, X-ray analysis.

Diacylketene aminals (DKA) have been previously shown to be efficient chelating ligands.[1-3] Our interest in DKA is also due to the possibility of the use of their complexes in heterocyclic syntheses.[4-7] Previous studies report on the crystal and molecular structures of diacetylketene *N*-benzoylaminal[2] and its difluoroboron chelate.[3] The molecular and crystal structures of the diphenylboron complex of 4-diaminomethylene-2-(*N*-benzoyl)diaminomethylene-1,3-cyclohexanedione has also been determined.[3]

Normally, the aminovinylcarbonyl fragment of DKA is involved in chelation and mononuclear boron complexes are formed, although ligands of this type are potentially tetradentate. It seemed that bicyclic compounds with two four-coordinated boron atoms could be most easily obtained from unsubstituted (at the nitrogen atom) DKA, 3-(diaminomethylene)pentane-2,4-dione (**1**). However, borylation of the latter by (butoxy)diphenylborane in boiling benzene affords only the mononuclear chelate **2**[8] (Scheme 1).

Scheme 1



It has been shown in the present study that when (butylthio)diphenylborane (2 eq.) is used as a borylating agent one can obtain binuclear complex **3** from **1** under mild conditions. Chelate **2** also readily transforms into complex **3** under the action of Ph_2BSBu. Apparently, the ability of the free NH_2 group in chelate **2** to form a B—N bond is weaker than that in ligand **1** and, therefore, a more reactive borylating agent, such as Ph_2BSBu, is required to obtain complex **3**. The structure of the bicyclic compound **3** has been confirmed by the methods of IR and ^1H and ^{11}B NMR spectroscopy and mass spectrometry. Unlike that of the unsymmetrical mononuclear complex **2**, the ^1H NMR spectrum of bis-chelate **3** exhibits one singlet from both Me-groups and one broadened singlet from the protons of the HNCNH fragment, which seemingly indicate that the two boron-containing six-membered rings are equivalent. In this connection, a more detailed study of the structure of binuclear chelate **3** appears to be of interest. Therefore, we studied the crystal and molecular structures of this compound by X-ray analysis. Figure 1 shows a general view of bis-chelate **3**. Its geometric parameters are presented in Table 1.

The remarkable feature of molecule **3** is that the formally identical B-chelate rings have in fact different structures. Thus, the six-membered ring including the B(1)—N(1)—C(1)—C(2)—C(3)—O(1) atoms (*A*) is virtually planar (deviations of the atoms from the middle plane of the cycle do not exceed 0.06 Å). The second ring with the B(2)—N(2)—C(1)—C(2)—C(4)—O(2) atoms (*B*) has a conspicuous twist—sofa conformation. In the apex of a deflected corner resides the N(2) atom, which is deviated from the middle plane of ring *B* by −0.292 Å. The dihedral *A*/*B* angle is 13.7°. The phenyl substituents form the following angles with the

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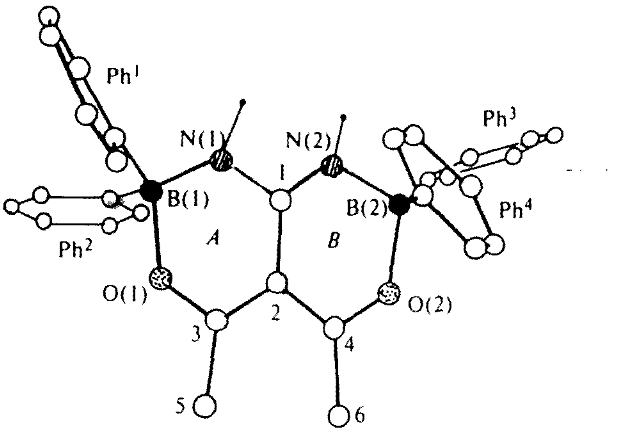


Fig. 1. Molecular structure and conformation of binuclear chelate 3.

Table 1. Bond lengths (*d*) and valence angles (ω) in molecule 3

Bond	*d*/Å	Bond	*d*/Å
B(1)—N(1)	1.530(9)	B(2)—N(2)	1.571(8)
B(1)—O(1)	1.525(8)	B(2)—O(2)	1.536(9)
N(1)—C(1)	1.344(7)	N(2)—C(1)	1.285(7)
C(2)—C(3)	1.386(9)	C(2)—C(4)	1.432(8)
O(1)—C(3)	1.316(7)	O(2)—C(4)	1.253(8)
C(3)—C(5)	1.494(9)	C(4)—C(6)	1.484(10)
B(1)—C(7)	1.611(10)	B(2)—C(19)	1.619(10)
B(1)—C(13)	1.621(11)	B(2)—C(25)	1.621(11)
C(1)—C(2)	1.475(9)		

Angle	ω/deg	Angle	ω/deg
O(1)—B(1)—N(1)	105.6(7)	O(2)—B(2)—N(2)	102.6(7)
O(1)—B(1)—C(7)	105.4(7)	O(2)—B(2)—C(19)	107.5(8)
O(1)—B(1)—C(13)	105.8(7)	O(2)—B(2)—C(25)	105.8(8)
N(1)—B(1)—C(7)	109.6(8)	N(2)—B(2)—C(19)	112.0(9)
N(1)—B(1)—C(13)	112.0(1)	N(2)—B(2)—C(25)	108.1(9)
C(7)—B(1)—C(13)	117.4(9)	C(19)—B(2)—C(25)	119.3(9)
C(1)—N(1)—C(1)	126.9(8)	B(2)—N(2)—C(1)	121.3(8)
B(1)—O(1)—C(3)	127.5(7)	B(2)—O(2)—C(4)	124.3(7)
N(1)—C(1)—C(2)	117.0(8)	N(2)—C(1)—C(2)	122.7(8)
C(1)—C(2)—C(3)	123.2(8)	C(1)—C(2)—C(4)	116.3(8)
O(1)—C(3)—C(2)	118.4(8)	O(2)—C(4)—C(2)	119.9(8)
O(1)—C(3)—C(5)	111.5(9)	O(2)—C(4)—C(6)	112.2(8)
C(2)—C(3)—C(5)	130.0(10)	C(2)—C(3)—C(6)	127.8(9)
N(1)—C(1)—N(2)	120.2(8)	C(3)—C(2)—C(4)	120.3(9)

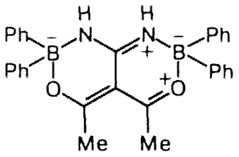
corresponding B-chelate rings: 107.4° (*A*/Ph^1), 94.5° (*A*/Ph^2) and 84.3° (*B*/Ph^3), 96.4° (*B*/Ph^4). In this case, the benzene rings themselves are turned relative to one another by 58.6° (Ph^1/Ph^2) and 64.7° (Ph^3/Ph^4).

The distribution of the bond lengths in the chelate rings *A* and *B* is also essentially different. Thus, the C(1)—N(1) (1.344 Å), C(3)—O(1) (1.314 Å), and C(2)—C(3) (1.389 Å) distances in ring *A* are characteristic for delocalized multiple bonds and are comparable with analogous distances found for monochelate complexes of boron with diacylketene aminals.[3] By contrast, the C(1)—N(2) (1.285 Å) and C(4)—O(2) (1.253 Å) bonds in ring *B* are more localized and close to the corresponding standard double bonds, whereas the C(2)—C(4) (1.432 Å) distance is closer to the ordinary C_{sp^2}—C_{sp^2} bond. The C(1)—C(2) (1.475 Å) bond is common to both rings and is therefore lengthened to a much greater extent than that in free α-oxoketene aminals[2] and their boron chelates.[3] The N—B bond in ring *B* is also noticeably longer than that in ring *A* (1.571 Å and 1.530 Å, respectively).

The significant distinction in the valence angles at the oxygen atoms is worthy of note: this angle in ring *A* is increased to 127.5° *vs.* 121.3° in *B*.

Consequently, the chelate rings *A* and *B* differ from one another both in their conformations and in the distribution of their bond lengths and valence angles. Apparently, this is due to the fact that, when forming the fused system, certain steric hindrances arise due to the proximity of bulky methyl groups. Indeed, if ring *B* in complex **3** were to have the same structure as *A* (*i.e.*, the molecule would be fully symmetrical relative to the C(1)—C(2) bond), then the C(5)...C(6) distance would be 2.40 Å, whereas, in the real molecule, it is increased to 3.00 Å, owing to the considerable distortion of ring *B*.

Hence, the structural formula **3** presented in Scheme 1 inadequately reflects the crystal-state structure of the chelate studied. However, any representation of its structure with localized multiple bonds corresponds to the data obtained to even a lesser degree. Nevertheless, giving a preference to formula **3**, one should note the contribution of betainic structure **3A**.



3A

No intermolecular contact distances less than the sums of the van der Waals radii of the corresponding pairs of atoms, were found in the crystal structure of **3**.

Experimental

^1H and ^{11}B NMR spectra were recorded on «Bruker WM-250» and «Bruker AC-200 P» instruments, respectively. IR spectra were registered on a UR-20 spectrophotometer in $CHCl_3$. The mass spectrum was obtained on a «Varian MAT-311 A» (electron impact, 70 eV).

(Butylthio)diphenylborane was obtained by redistribution of an equimolar mixture of $BuOBPh_2$ and $BuSBBu_2$ with slow distillation and collection of the fraction with b.p. 145—150 °C (2 Torr) (*cf.* lit.:[9] 180 °C (7 Torr)). The yield was 65%.

Diphenylboron chelate 2 was synthesized using a previously reported procedure.[8]

Bis-diphenylboron chelate of 3-(diaminomethylene)pentane-2,4-dione (3). a. A mixture of aminal **1** (1.42 g, 10 mmol) and Ph_2BSBu (5.2 g, 20.4 mmol) in 20 ml of THF was stirred

Table 2. Atomic coordinates in molecule **3** (for nonhydrogen atoms $\times 10^4$, for hydrogen atoms $\times 10^3$)

Atom	*x*	*y*	*z*
O(1)	1177(1)	2168(1)	1399(2)
O(2)	2140(1)	2658(1)	−0955(2)
N(1)	2132(2)	2212(2)	1504(3)
N(2)	2593(1)	2340(2)	0287(2)
C(1)	2159(2)	2320(2)	0685(3)
C(2)	1668(2)	2416(2)	0234(3)
C(3)	1194(2)	2326(2)	0619(3)
C(4)	1714(2)	2646(2)	−0576(3)
C(5)	0664(2)	2339(3)	0238(3)
C(6)	1290(3)	2902(3)	−1053(4)
C(7)	1625(2)	1544(3)	2366(3)
C(8)	1394(3)	1128(3)	1930(4)
C(9)	1389(4)	0629(4)	2209(5)
C(10)	1645(4)	0511(3)	2943(6)
C(11)	1879(4)	0900(4)	3403(5)
C(12)	1865(3)	1415(3)	3125(4)
C(13)	1541(2)	2587(3)	2685(3)
C(14)	1699(3)	3100(3)	2509(4)
C(15)	1610(4)	3504(3)	3057(6)
C(16)	1318(4)	3399(4)	3801(6)
C(17)	1160(3)	2924(3)	3970(4)
C(18)	1266(2)	2560(3)	3428(3)
C(19)	2566(2)	1780(3)	−1091(3)
C(20)	2443(4)	1722(3)	−1935(4)
C(21)	2383(4)	1241(4)	−2291(5)
C(22)	2441(4)	0796(4)	−1818(7)
C(23)	2568(4)	0845(4)	−1001(6)
C(24)	2611(4)	1322(3)	−0646(4)
C(25)	3133(2)	2697(2)	−0951(3)
C(26)	3219(3)	3180(3)	−0566(4)
C(27)	3639(4)	3475(4)	−0796(5)
C(28)	3963(4)	3329(5)	−1448(6)
C(29)	3875(4)	2861(5)	−1832(5)
C(30)	3448(3)	2556(3)	−1598(4)
B(1)	1632(3)	2134(3)	2006(4)
B(2)	2628(3)	2355(3)	−0691(4)
H(N(1))	251(2)	223(3)	176(3)
H(N(2))	291(5)	222(5)	052(7)

for 3 h under an Ar atmosphere. The solvent was distilled off under reduced pressure, and the residue was treated with hexane and filtered to obtain 4.09 g (87%) of chelate **3**, b.p. 139—141 °C (benzene—hexane, 1:3). Found (%): C, 76.85; H, 5.74; B, 4.47; N, 6.08. $C_{30}H_{28}B_2N_2O_2$. Calculated (%): C, 76.63; H, 6.00; B, 4.60; N, 5.96. Mass spectrum, *m/z*: 393 $[M-Ph]^+$. ^1H NMR ($CDCl_3$, δ, ppm): 2.54 (s, 6 H, 2 Me); 5.15 (br.s, 2 H, 2 NH); 7.23—7.56 (m, 20 H, 4 Ph). ^{11}B NMR ($CHCl_3$, δ, ppm): 1.7. IR ($CHCl_3$, ν/cm^{-1}): 3400, 3355 br. (NH); 1630 v.s, 1570, 1555.

b. Analogously to the foregoing experiment, from 1.75 g (5.7 mmol) of chelate **2** and 1.5 g (5.9 mmol) of Ph_2BSBu were obtained 2.52 g (94%) of the binuclear complex **3**.

X-ray study of binuclear chelate 3. Colorless crystals of compound **3** were grown from a benzene—hexane (1:1) mixture. The unit cell parameters and a set of experimental reflections with $I > 2\sigma(I)$ were obtained on an automated RED-4 four-circle diffractometer (Cu-K_α radiation, graphite monochromator, θ/2θ-scanning). The crystals are tetragonal: $a = b = 25.702(3)$, $c = 16.034(2)$ Å, $V = 10592.9$ Å^3, space group $I4_1/a$, $C_{30}H_{28}B_2N_2O_2$. The structural calculation included 1459 independent reflections. The structure was deciphered by a direct method, the coordinates of the nonhydrogen atoms were refined by the least-squares method in an anisotropic approximation, and those of the hydrogen atoms were refined in an isotropic approximation. The calculations were performed using the AREN-90[10] program. The final value of *R* was 0.065. The coordinates of the nonhydrogen atoms are given in Table 2.

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