Letter

Structure and spectroscopic characteristics of 2′-diethylboryl-4″-dimethylaminochalcone bearing an intramolecular boron–oxygen coordinate bond

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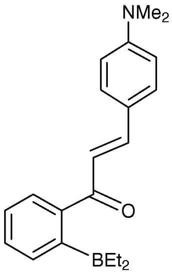
How formation of an intramolecular coordinate bond affects the molecular structure was examined in the structural comparison of 2′-diethylboryl-4″-dimethylaminochalcone (1) and 2′-ethylenedioxyboryl-4″-dimethylaminochalcone (2) with chloro{2-[(4-dimethylaminostyryl) carbonyl]phenyl}(4-methylphenyl)]bismuthane (3) and 4″-dimethylaminochalcone (4).

It is an important issue for us to examine how coordination affects molecular structure and properties. In preceding papers[1] we reported a marked structural change in the non-alternant ligand of low resonance energy by formation of coordinate bonds with a diethylboryl group in comparison with the alternant ligands.[1b] Herein we disclose how the intramolecular coordinate bond affects the synthetic, structural, and spectral features of 4″-dimethylaminochalcone chromophore.



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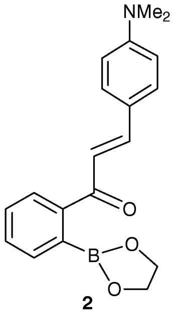

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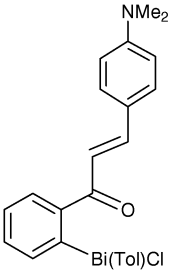

Tol = 4-MeC$_6$H$_4$

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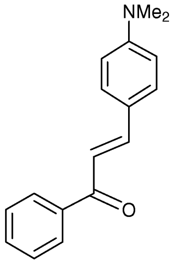

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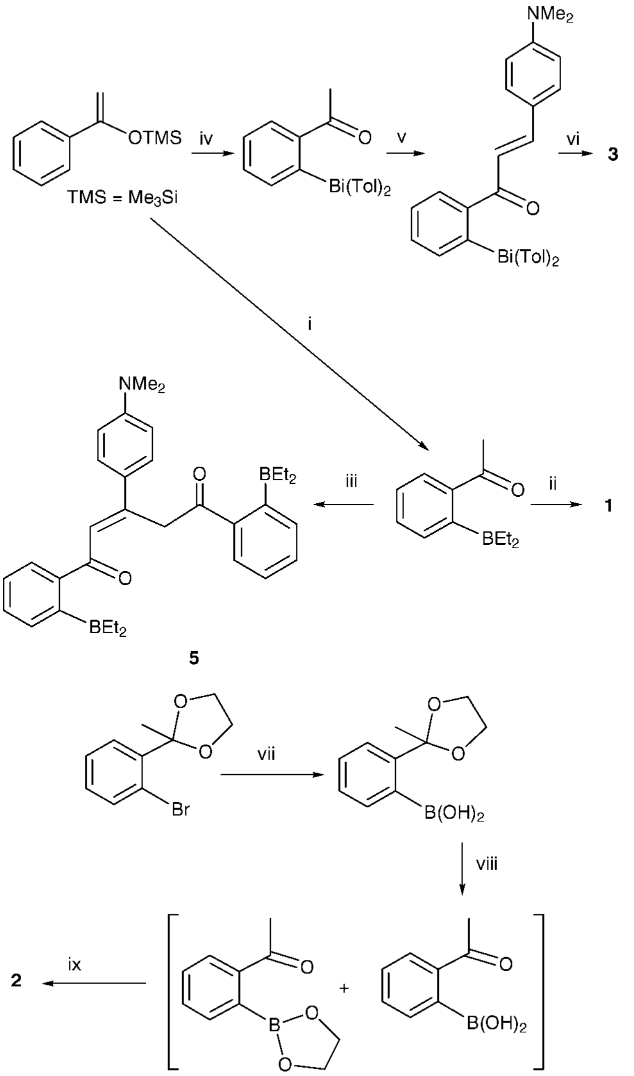
The synthetic routes to 2′-diethylboryl-4″-dimethylaminochalcone (**1**), 2′-ethylenedioxyboryl-4″-dimethylaminochalcone (**2**) and chloro{2-[(4-dimethylaminostyryl)carbonyl]phenyl}(4-methylphenyl)]bismuthane (**3**)[2] are shown in Scheme 1.† Three experimental findings should be stressed in comparison to the simple synthesis of **4** from 4-dimethylaminobenzaldehyde (DMAB) and acetophenone with potassium hydroxide. Firstly, the aldol reaction of 2′-diethylborylacetophenone and DMAB with lithium diisopropylamide proceeded to give **1** despite the presence of a trivalent boron atom having a high affinity for bases. Secondly, when potassium *tert*-butoxide in a mixture of benzene and *tert*-butanol was used, 2 equiv. of 2′-diethylborylacetophenone added to DMAB, giving the undesired product **5** in moderate yield, contrasting with the synthesis of **4**. Thus, due to the intramolecular coordinate bond, the β-hydroxy intermediate in the aldol condensation easily suffered from dehydroxylation, followed by nucleophilic attack of the second enolate of 2′-diethylborylacetophenone. Thirdly, upon attempted deacetalization of the carbonyl group with *p*-toluene sulfonic acid in the synthesis of **2**, transacetalization to the boron atom efficiently took place. Thus, protection of the acidic hydrogens of the hydroxy groups could be omitted in the subsequent aldol condensation employing basic conditions.

While **4** is yellow crystals, compounds **1**, **2**, and **3** are reddish-violet, reddish-violet and greenish yellow crystals, respectively. The longest wavelength absorption band of the UV/VIS spectrum of **1** in acetonitrile shows an 86 nm bathochromic shift similar to that of **3**, compared to **4**.‡ Since the large bismuth atom would be placed more closely to the oxygen atom of the carbonyl group, the high Lewis acidity of the diethylboryl group is responsible for this similar bathochromic shift. On addition of amines, such as triethylamine, the color of a solution of **1** turns yellow, indicating that the intramolecular boron–oxygen coordinate bond is cleaved with formation of an intermolecular boron–nitrogen coordinate bond. The change is irreversible and results in decomposition when dilute aqueous hydrochloric acid is added to remove the amine.

The spectrum of **2** shows two bands in the regions of the longest wavelength absorption bands of **1** and **4**, indicating a weaker Lewis acidity of the ethylenedioxyboryl group than that of the diethylboryl group. Compound **1** is moderately fluorescent with an emission maximum at 576 nm (excitation at 494 nm).[3]

The solvatochromism of the longest wavelength absorption bands is noteworthy, although the shift dependences on solvent polarity not large.§ Thus, when the solvent is changed from cyclohexane to methanol a bathochromic shift of 23 nm is observed for **1**. A linear solvation energy relationship (LSER) [$\nu(\mathbf{1}) = 21.555 - 1.692\pi^*$] is obtained between the solvent shifts and the Kamlet–Taft parameter π^*[4] where $n = 11$, $R = 0.948$ and $\sigma = 0.139$ kK, including both protic



Scheme 1 Reagents and conditions: (*i*) Bu^{n}Li (3 equiv.), TMEDA (3 equiv.), hexane, RT, 24 h, then Et$_2$BOMe (2 equiv.), RT, 30 min; brine, 74.7%; (*ii*) LDA (1.1 equiv.), DMAB (1 equiv.), Et$_2$O, RT, 45 min; brine, 39.3%; (*iii*) DMAB (1 equiv.), Bu^{t}OK (1.3 equiv.), C$_6$H$_6$–Bu^{t}OH (1:1 v/v), RT, 3 h, 30.3%; (*iv*) Bu^{n}Li (3 equiv.), TMEDA (3 equiv.), hexane, RT, 24 h, then Tol$_2$BiCl (1 equiv.), RT, 1 h; brine, 39.4%; (*v*) DMAB (1.3 equiv.), Bu^{t}OK (1.3 equiv.), C$_6$H$_6$–Bu^{t}OH (10:3 v/v), RT, 4 h, 77.6%; (*vi*) BF$_3$·OEt$_2$ (3 equiv.), C$_6$H$_6$, ice cooling; brine, 87.7%; (*vii*) Bu^{n}Li (1 equiv.), B(OPr^i)$_3$ (1 equiv.), THF, −78 °C to RT, 80 min; brine, 83.3%; (*viii*) TsOH (0.01 equiv.), acetone, 45 min, then removal of acetone; (*ix*) DMAB (1 equiv.), Bu^{t}OK (3 equiv.), THF–Bu^{t}OH (1:1 v/v), 0 °C, 15 min; brine, then conc. HCl–MeOH (1:1 v/v), 24 h, neutralization with NaHCO$_3$, 27.6%.

and aprotic solvents. A larger bathochromic shift of 33 nm is observed from the same solvent change for **4**. However, in contrast to **1**, two separate LSERs [$\nu(\mathbf{4}) = 25.994 - 2.256\pi^*$ and $\nu(\mathbf{4}) = 24.730 - 1.448\pi^*$] are obtained where $n = 8$, $R = 0.931$ and $\sigma = 0.263$ kK or $n = 3$, $R = 0.995$ and $\sigma = 0.012$ kK for aprotic or protic solvents, respectively, due to the deviation of the absorption maxima in protic solvent in the longer wavelength regions. If the hydrogen-bond donor parameter α is included, the behavior for **4** is described by a single LSER, that is, $\nu(\mathbf{4}) = 25.924 - 1.993\pi^* - 0.989\alpha$ where $n = 11$, $R = 0.957$ and $\sigma = 0.232$ kK.

The fluorescence spectra of **1** and **4** display solvatochromism as well.¶ For example, when the solvent is changed from carbon tetrachloride to ethanol, bathochromic shifts of 50 and 96 nm are obtained for **1** and **4**, respectively. A Kamlet–Taft approach works for the fluorescence study as well. Thus, $\nu(\mathbf{1}) = 19.684 - 2.844\pi^*$ and $\nu(\mathbf{4}) = 22.929 - 4.432\pi^* - 2.33\alpha$ are obtained where $n = 10$, $R = 0.805$ and $\sigma = 0.387$ kK or $n = 10$, $R = 0.953$ and $\sigma = 0.477$ kK for **1** or **4**, respectively. Hence, it can be concluded that, when compared with the respective ground states, the increasing polarity of the excited state of **4** is greater than that of **1** by the greater value of the π^* coefficient. According to the Lippert–Mataga equation,[5] the shifts in various solvents and a measure for solvent polarity defined as $(\varepsilon - 1)/(2\varepsilon + 1) - (n^2 - 1)/(2n^2 + 1)$ also give a good linear relationship for both compounds ($Y = 1.7168 + 3.6745X$ and $Y = 2.8469 + 8.9390X$ where $n = 10$, $R = 0.963$ and $\sigma = 0.0994$ kK or $n = 10$, $R = 0.950$ and $\sigma = 0.282$ kK for **1** or **4**, respectively), exhibiting a more pronounced polarity in the excited state than in the ground state in both compounds. Since the Onsager effective radii[6] for **1** and **4** are estimated from the volume taken from the X-ray structure analysis[7] of **4** to be 4.35 Å, the differences between the dipole moment vector of the excited state and that of the ground state $|\mu_e - \mu_g|$ are calculated to be 5.48 and 8.55 D, respectively.

These spectroscopic characteristics are well interpreted by the intramolecular boron–oxygen coordinate bond, which prevents positive hydrogen-bond formation between protic solvents and the oxygen atom placed at the end of the chromophore.

A single-crystal X-ray crystallographic study at −120 °C reveals the enhanced coplanarity of the skeletal atoms, all the skeletal atoms of **1** being coplanar with a maximum deviation of only 3° (Figs. 1 and 2).‖ The intramolecular coordinate bond between the boron and oxygen atoms, together with the charge transfer from the dimethylamino group to the carbonyl

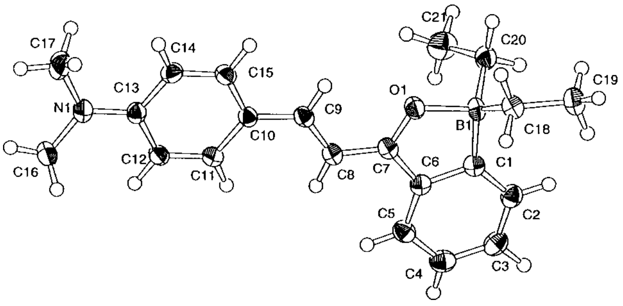


Fig. 1 Computer-generated thermal ellipsoid of **1**. Some important bond distances (Å) and dihedral angles (°) are as follows: B1–O1 1.608(2), B1–C1 1.616(3), C1–C6 1.408(3), C6–C7 1.455(3), C7–O1 1.294(2), C7–C8 1.424(3), C8–C9 1.367(3), C9–C10 1.434(3), C10–C11 1.411(3), C10–C15 1.405(3), C11–C12 1.372(3), C12–C13 1.420(3), C13–C14 1.412(3), C14–C15 1.372(3), C13–N1 1.359(2), O1–C7–C6–C1 −0.1(2), C1–B1–O1–C7 −3.0(2), C6–C7–C8–C9 −177.0(2), C7–C8–C9–C10 177.5(2), C8–C9–C10–C11 −2.6(3), C12–C13–N1–C16 6.1(3), C12–C13–N1–C17 −176.9(2).

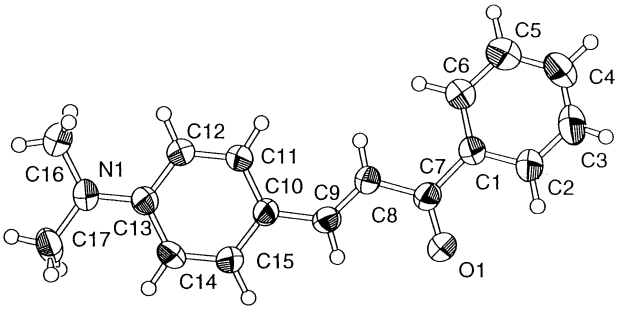


Fig. 2 Computer-generated thermal ellipsoid of **4**. Some important bond distances (Å) and dihedral angles (°) are as follows: C1–C2 1.385(5), C1–C7 1.488(4), C7–O1 1.231(4), C7–C8 1.464(4), C8–C9 1.337(4), C9–C10 1.452(4), C10–C11 1.400(4), C10–C15 1.403(4), C11–C12 1.384(4), C12–C13 1.413(4), C13–C14 1.401(4), C14–C15 1.382(4), C13–N1 1.372(4), O1–C7–C1–C2 −19.0(5), C1–C7–C8–C9 177.3(3), C7–C8–C9–C10 −176.6(3), C8–C9–C10–C11 −2.1(6), C12–C13–N1–C16 −3.1(5), C12–C13–N1–C17 −176.9(4).

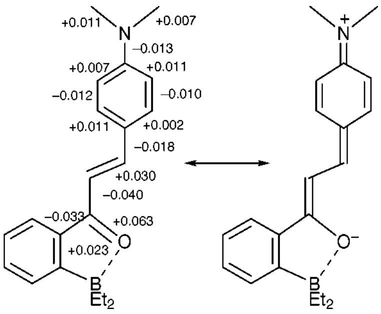


Fig. 3 Bond distances changed by the intramolecular coordinate bond and contributing charge transfer electronic structure of **1**: elongated bond distances denoted by a plus and shortened bond distances denoted by a minus, compared with **4**.

group, seems to be responsible for the coplanarity. Thus, as shown in Fig. 1, the shortened distance between the boron and oxygen atoms [1.608(2) Å] clearly exhibits the formation of the intramolecular coordinate bond. The difference between the corresponding bond distances of **1** and **4**, shown in Fig. 3, is indicative of the contribution from the canonical structure with the charge transfer electronic structure. In particular, the increased double bond character of the bonds between C7 and C8, and C9 and C10 is deduced from the respective shortened bond distances.

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Notes and references

† All the compounds were identified spectroscopically and by means of high resolution mass spectrometry. NMR (CDCl$_3$) **1**: ^{1}H δ 0.65–0.69 (10H, m, Et$_2$B), 3.11 (6H, s, Me$_2$N), 6.72 (2H, d, $J_{AB} = 9.2$, Me$_2$NAr*H*), 7.30 (1H, t, $J = 7.9$, BArH), 7.39 (1H, d, $J_{AB} = 15.3$, CH=C*H*CO), 7.51 (1H, t, $J = 7.9$, BArH), 7.66 (2H, d, $J_{AB} = 9.2$, Me$_2$NAr*H*), 7.68 (1H, d, $J = 7.3$, BArH), 8.00 (1H, d, $J = 7.9$, BArH), 8.28 (1H, d, $J_{AB} = 15.3$, C*H*=CHCO); ^{13}C δ 10.0, 14.8, 40.1, 108.6, 119.9, 122.2, 125.1, 125.7, 128.9, 131.9, 132.4, 132.8, 137.9, 150.5, 153.3, 192.5; ^{11}B δ 14.8. **2**: ^{1}H δ 3.10 (6H, s, Me$_2$N), 4.34 (4H, s, CH$_2$CH$_2$), 6.71 (2H, d, $J_{AB} = 9.2$, Me$_2$NAr*H*), 7.33 (1H, d, $J_{AB} = 15.3$, CH=C*H*CO), 7.44 (1H, t, $J = 7.3$, BArH), 7.58 (1H, t, $J = 7.3$, BArH), 7.62 (2H, d, $J_{AB} = 9.2$, Me$_2$NAr*H*), 7.70 (1H, d, $J = 7.3$, BArH), 7.93 (1H, d, $J = 7.9$, BArH), 8.18 (1H, d, $J_{AB} = 15.3$, C*H*=CHCO). **3**: ^{1}H δ 2.22 (3H, s, Me), 3.10 (6H, s, Me$_2$N), 6.70 (2H, d, $J_{AB} = 8.5$, Me$_2$NAr*H*), 7.30 (2H, d, $J_{AB} = 7.9$, MeAr*H*), 7.51 (1H, d, $J_{AB} = 15.3$, CH=C*H*CO), 7.61 (2H, d, $J_{AB} = 8.5$, Me$_2$NAr*H*), 7.62 (1H, t, $J = 7.3$, BiArH), 7.94 (1H, t, $J = 7.3$, BiArH), 8.06 (2H, d, $J_{AB} = 7.9$, MeAr*H*), 8.08 (1H, d, $J_{AB} = 15.3$, C*H*=CHCO), 8.41 (1H, d, $J = 7.3$, BiArH), 9.11 (1H, d, $J = 7.3$, BiArH). **5**: ^{1}H δ 0.49–0.55 (20H, m, Et$_2$B), 3.07 (6H, s, Me$_2$N), 5.31 (2H, s, CH$_2$), 6.70 (2H, d, $J_{AB} = 8.6$, Me$_2$NAr*H*), 7.31 (1H, t, $J = 7.5$, BArH), 7.35 (1H, t, $J = 7.0$, BArH), 7.51 (1H, t, $J = 7.5$, BArH), 7.58 (1H, t, $J = 7.5$, BArH), 7.59 (1H, s, COCH), 7.64–7.66 (4H, m, ArH), 8.03 (1H, d, $J = 7.9$, BArH), 8.16 (1H, d, $J = 7.9$, BArH).

‡ UV/VIS (acetonitrile) λ_{max}/nm (log ε): **1**: 292 (4.09), 494 (4.72); **2**: 264 (4.08), 434 (4.27), 500 sh (4.12); **3**: 285 (4.19), 484 (4.68); **4**: 262 (4.22), 328 (3.69), 408 (4.45).

§ Solvatochromism in the longest wavelength absorption bands of **1** and **4** (nm): cyclohexane (464, 386), Et$_2$O (478, 390), CCl$_4$ (468, 394), Pr^{i}OH (481, 416), EtOH (486, 418), AcOEt (486, 402), THF (490, 405), MeOH (487, 419), CH$_3$CN (494, 408), CHCl$_3$ (486, 414), CH$_2$Cl$_2$ (492, 414).

¶ Solvatochromism of the fluorescence of **1** and **4** (nm): CCl$_4$ (512, 449), CHCl$_3$ (546, 505), Et$_2$O (533, 465), AcOEt (552, 493), THF (559, 485), CH$_2$Cl$_2$ (559, 520), Pr^{i}OH (559, 542), EtOH (562, 545), CH$_3$CN (576, 530), MeOH (563, 546).

‖ Data were collected at 153 K on a Rigaku AFC7R diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å) and a rotating anode generator. The structure was solved by direct methods. The non-hydrogen atoms were refined anisotropically. Crystal data for **1**: $C_{21}H_{26}BNO \cdot 1.5_6H_6$, $M = 436.42$, red, prismatic crystal (0.20 × 0.40 × 0.80 mm), triclinic, $P\bar{1}$ (#2), $a = 9.622(4)$, $b = 15.155(5)$, $c = 9.522(3)$ Å, $\alpha = 101.21(3)$, $\beta = 95.90(4)$, $\gamma = 108.32(3)°$, $U = 1272.9(9)$ Å^3, $Z = 2$, $D_c = 1.139$ g cm^{-3}, $\mu = 0.67$ cm^{-1}, $F(000) = 470$. The final cycle of full-matrix least-squares refinement was based on 3338 observed reflections [$I > 3.00\,\sigma(I)$] and 438 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.040$ and $R_w = 0.046$. Crystal data for **4**: $C_{17}H_{17}NO$, $M = 251.33$, yellow, prismatic crystal (0.20 × 0.40 × 0.60 mm), monoclinic, $P2_1/a$ (#14), $a = 9.491(4)$, $b = 11.884(3)$, $c = 12.912(3)$ Å, $\beta = 108.35(2)°$, $U = 1382.3(7)$ Å^3, $Z = 4$, $D_c = 1.208$ g cm^{-3}, $\mu = 0.75$ cm^{-1}, $F(000) = 536$. The final cycle of full-matrix least-squares refinement was based on 1347 observed reflections [$I > 3.00\,\sigma(I)$] and 241 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.051$ and $R_w = 0.065$. CCDC reference number 440/119. See http://www.rsc.org/suppdata/nj/1999/683/ for crystallographic files in .cif format.

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