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Synthesis, structures and luminescent behaviour of tridentate salicylaldiminato-type borate complexes

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Dedicated to Professor Jonathan Dilworth on the occasion of his 65th birthday.

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ABSTRACT

Treatment of the ligands $3,5-tBu_2-2-(OH)C_6H_2CHNR$ [R = $2-(CO_2H)C_6H_4$ (**1a**) and $2-(CO_2H)C_{10}H_6$ (**1b**)] with trimethylborate, B(OMe)_3, in toluene yields, after work-up, the yellow crystalline complexes {[$3,5-tBu_2-2-(O)C_6H_2CHNR$]B(OMe)} [R = $2-(CO_2)C_6H_4$ (**2a**) and $2-(CO_2)C_{10}H_6$ (**2b**)], respectively. Further treatment of these complexes with trifluoromethanesulfonic (triflic) acid, CF₃SO₃H, followed by recrystallisation from tetrahydrofuran (thf) afforded the triflate salts [$3,5-tBu_2-2-(O)C_6H_2CHNR$]B(thf)][CF₃SO₃] [R = $2-(CO_2)C_6H_4$ (**3a**) and $2-(CO_2)C_{10}H_6$ (**3b**)]. An electroluminescent device was constructed using **2a**, which produced orange-green light with broad emission spectra (maximum brightness of 5 cd/m² being observed at 13 V). Compounds **1a** and **2b**-2MeCN have been characterised by single crystal X-ray structure determinations.

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1. Introduction

In recent years there has been considerable interest in the use of chelate ancillary ligands in complexes to be used for electroluminescent displays, in-part because these ligands afford high stability and volatility [1]. This is particularly the case for boron(III)-based organic light emitting devices (OLEDs), which generally exhibit increased stability when compared with their aluminium counterparts. Of particular note is the use of 'tunable' nitrogen/oxygen chelate donor ligands, such as quinolates and related species to form monomeric complexes (see I–V, Chart 1), by Wang et al. [2] and others. [3] More recent work by Ko et al. has utilized oxazolylphenolate ligands, which on reaction with BPh₃ afford complexes of the form VI. An electroluminescence device was constructed for Ar = NPh₂, and possessed a maximum brightness of 2905 cd/ m² at 13 V [4], whilst the use of Ar = 4-cyanophenyl, 2,4-difluorophenyl, 4-chlorophenyl, phenyl, 4-methoxyphenyl and 4-dimethylaminophenyl allowed the system to be tuned from blue to green. Other research groups have extended this methodology to include organoboron polymers [5].

We have been investigating the chemistry of the Schiff-base ligand $3,5-tBu_2-2-(OH)C_6H_2CHNC_6H_4-2-(CO_2H)$ (1a, see Chart 2) towards group 13 reagents [6]. We have now extended our

investigations to boron and describe herein the synthesis and structures of the borate complexes {[$3,5-tBu_2-2-(O)C_6H_2CHNR$]B-(O Me)} [R = 2-(CO_2)C_6H_4 (**2a**) and 2-(CO_2)C_{10}H_6 (**2b**)] together with the synthesis of the triflate salts [{ $3,5-tBu_2-2-(O)C_6H_2CHNR$ }B(thf)] [CF₃SO₃] [R = 2-(CO₂)C₆H₄ (**3a**) and 2-(CO₂)C₁₀H₆ (**3b**)].

The behaviour of the borates **2a** and **2b** towards UV light has been examined and an electroluminescent device made utilizing complex **2a**. We note that the electroluminescent behaviour of some Schiff-base born complexes (see Chart 3) have recently been reported [7], whilst a series of mononuclear Schiff-base borates and boron halides (Chart 4) have been reported, the latter being used to dealkylate trimethyl phosphate [8].

2. Results and discussion

The ligands **1a** and **b** were prepared via the condensation reaction between 3,5-di-*tert*-butylsalicyladimine and anthranilic acid, 1,2-(NH₂)(CO₂H)C₆H₄, or 3-amino-2-napthoic acid, 2-(CO₂H),3-(NH₂)C₁₀H₆, as pale yellow solids in good yield (typically *ca.* 75% isolated yield). The ¹H NMR spectra of these ligands exhibit resonances in the regions $\delta \sim 11.6$ for the OH (disappears on D₂O addition) and ~9.9 ppm for the CO₂H, respectively (shifts being affected by the extensive H-bonding discussed below). In the IR spectrum, the characteristic t(C=N) imine stretch is tentatively assigned to the weak absorption at 1612 cm⁻¹. A single crystal X-ray structure



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of **1a** shows (Fig. 1) the molecule exhibits both inter- and intra-molecular hydrogen bonding. The former involves the imine nitrogen centre and the hydroxyl group such that $H(1)\cdots N(1) = 1.83$ Å with angle $O(1)-H(1)\cdots N(1) = 148^{\circ}$. The inter-molecular H-bond is of similar strength and involves carboxylic acid groups in neighbouring molecules: the $H(3)\cdots O(2A)$ distance is 1.81 Å with an angle $O(3)-H(3)\cdots O(2A)$ of 174°. There is only a small (*ca.* 4.8°) out of plane rotation of the C=N double bond relative to the phe-

Chart 2.

nolic ring, whilst the anthranilic acid derived ring is orientated 54.6° to the phenolic ring plane. Bond lengths and angles for **1a** are presented in Table 1; crystallographic data are given in Table 3.

Treatment of **1a** and **1b** with excess trimethylborate, $B(OMe)_3$, in refluxing toluene affords the corresponding borate complexes {[3,5-*t*Bu₂-2-(O)C₆H₂CHNR]B(OMe)} [R = 2-(CO₂)C₆H₄ (**2a**) and 2-(CO₂)C₁₀H₆ (**2b**)]. Both **2a** and **2b** can be obtained in good yields (50–60%) as yellow crystalline solids on prolonged standing at 0 °C. In the ¹H NMR spectrum, the imine resonances fall in the 8.8–8.9 ppm range, whilst in the ¹¹B NMR spectrum of each complex, the one resonance is found at δ 5.53 (**2a**) and 5.73 ppm (**2b**)



Chart 3.



Fig. 1. Crystal structure of 1a emphasizing (a) intra-molecular H-bonding and (b) inter-molecular H-bonding.

Table 1Selected bond lengths (Å) and angles (°) for 1a. Symmetry operator A = -x, 1-y, 1-z.

N(1)-C(15)	1.2781(10)
N(1)-C(16)	1.4123(10)
N(1)H(1)	1.83
O(2A)H(3)	1.81
O(1)-H(1)···N(1)	148
O(3)-H(3) ··O(2A)	174

consistent with 4-coordinate boron [3,4]. In the IR spectrum, the ν B–N absorption is found at 1019 (**2a**) and 1020 (**2b**) cm⁻¹.

The X-ray crystal structure of **2b** is shown in Fig. 2; bond lengths and angles are in Table 2 (for crystallographic data see Table 3). The boron centre has a tetrahedral geometry with near ideal O–B–N angles of 107.45(16)° and 109.40(14)° for each of the sixmembered rings. The B–O(2) distance [1.459(2) Å] is similar to those observed by Atwood for the related complex $[LB(OSiPh_3)]$ [1.465(7) and 1.433(7) Å] (where L is the tridentate, doubly deprotonated ligand derived from *N*-salicylidene-*o*-aminophenol) [9]. The distance to the oxygen derived from the acid is 1.467(2) Å. The B–N distance 1.566(3) Å is slightly shorter than that observed by Atwood [1.5998(8) Å]. The C=N bond of **2b** retains its double bond character, being 1.298(2) *cf* 1.2781(10) Å in the free ligand **1a**.



Fig. 2. Molecular structure of 2b.

 Table 2

 Selected bond lengths (Å) and angles (°) for 2b.

B(1)-N(1)	1.566(3)
B(1)-O(1)	1.424(3)
B(1)-O(2)	1.459(2)
B(1)-O(3)	1.467(2)
N(1)-C(2)	1.298(2)
B(1)-O(1)-C(1)	117.52(16)
B(1)-O(2)-C(4)	125.12(15)
B(1)-O(3)-C(17)	121.86(15)
B(1)-N(1)-C(2)	123.33(14)

There is currently much interest in group 13 compounds incorporating salen-type ligands [10a], and cationic species thereof [10b], primarily due to their application in catalysis. A facile entry into cationic chemistry is via the addition of the strong acid CF₃SO₃H (triflic acid) which is known to lead to cation–anion pair formation [9]. Similarly, for **2a** and **2b**, reaction with one equivalent of triflic acid in toluene followed by recrystallisation from toluene/tetrahydrofuran (10:1) afforded the triflate salts [{3,5-*t*Bu₂-2-(OC₆H₂CHNR}B(thf)][CF₃SO₃] [R = 2-(CO₂)C₆H₄ (**3a**) and 2-(CO₂)C₁₀H₆ (**3b**)]. Use of neat thf as solvent here is best avoided as **3a** and **3b** act as Lewis acid catalysts for the polymerization of thf. Such behaviour is unsurprising given that the related Atwood systems (and [ⁿBu₂BOTf] were shown to polymerize propyleneoxide via a proposed anionic mechanism [9].

Electrochemically complex **2a** undergoes three separate processes within the solvent window (Fig. 3). At positive potentials the complex undergoes an irreversible oxidation at 1.25 V. This is followed by a (quasi) reversible oxidation at higher potential, $E_{1/2} = 1.48$ V, $\Delta E_p = 0.12$ V. In the reverse scan an irreversible reduction occurs at -1.61 V. Variations in scan-rate, direction and limits do not reveal any other details; the first oxidation and the reduction remain completely irreversible.

Given the suitable physiochemical properties of **2a**, an EL device was fabricated. This device showed orange/green emission with an EL spectrum (see Fig. 4) consisting of a single broad peak with a maximum at 592 nm. The light output (not optimized) from the device, with a maximum brightness of 5 cd/m^2 being observed at 13 V, is poor and is far less impressive than that reported for

Table	3
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Summary of crystallographic data.

Compound	1a	2b·2MeCN
Formula	C ₂₂ H ₂₇ NO ₃	$C_{27}H_{30}BNO_4 \cdot 2(C_2H_3N)$
Formula weight	353.45	525.44
Crystal system	triclinic	monoclinic
Space group	ΡĪ	$P2_1/n$
a (Å)	6.8667(9)	11.1089(5)
b (Å)	10.8258(13)	9.4740(5)
c (Å)	13.3081(16)	29.0748(14)
α (°)	81.213(2)	90
β (°)	88.722(2)	98.9395(9)
γ (°)	84.492(2)	90
V (Å ³)	973.1(2)	3022.8(3)
Ζ	2	4
T (K)	150(2)	200(2)
Radiation, λ (Å)	0.71073	0.71073
Crystal size (mm ³)	$0.33 \times 0.15 \times 0.09$	$0.55 \times 0.20 \times 0.18$
θ_{range} (°)	1.91-28.89	2.09-28.87
Reflections measured	19 683	23 249
Unique reflections	18 882	6993
R _{int}	0.019	0.022
Reflections with $F^2 > 2\sigma(F^2)$	12 723	4361
Transmission factors		0.959, 0.986
Data/restraints/parameters	18 882/0/244	6993/54/361
$R_1 [F^2 > 2\sigma(F^2)]$	0.0442	0.0528
wR_2 (all data)	0.1188	0.1657
Goodness-of-fit (GOF), S	1.024	1.034
Largest difference peak and	0.341, -0.237	0.263, -0.191
hole (e Å ⁻³)		



Fig. 3. CV of 2a in dichloromethane.

devices made from other boron Schiff-base complexes such as **VII** (465 cd/m²), **VIII** (195 cd/m²) and **IX** (840 cd/m²). [7a,b] The spikes in Fig. 4 represent artifacts from the measurements and are due to small shorts in the device producing sparks of comparable brightness to the EL emission.

The PL spectrum of **2a** in solution (excitation wavelength = 350 nm) is broad with a maximum at 385 nm, has a smaller peak at around 510 nm and a broad tail into the red. To the eye, this complex appears to luminesce yellow in both solution and the solid state. These features are at higher energy than in the EL spectrum (a single broad peak centred at around 592 nm, see Fig. 4). The red-shift in emission is common in organic electroluminescence, but a detailed explanation of the photophysics of this complex remains as future work.

In conclusion, the compounds described herein provide a useful insight into the coordination environment afforded by the Schiffbase ligands [3,5- tBu_2 -2-(O)C₆H₂CHNR], where R = 2-(CO₂)C₆H₄ and 2-(CO₂)C₁₀H₆. The borates {[3,5- tBu_2 -2-(O)C₆H₂CHNR] B(OMe)}, upon irradiation by UV light, produce a bright yellow colour both in solution and in the solid-state, and an electroluminescent device was constructed using **2a** (R = 2-(CO₂)C₁₀H₆), which produced orange-green light with broad emission spectra (maximum brightness of 5 cd/m²).

3. Experimental

3.1. General

All manipulations were carried out under an atmosphere of nitrogen using standard Schlenk and cannula techniques or in a conventional nitrogen-filled glove-box. Solvents were refluxed over an appropriate drying agent, and distilled and degassed prior to use. Elemental analyses were performed by the microanalytical services of the School of Chemical Sciences at The University of East Anglia. NMR spectra were recorded on a Varian VXR 400 S spectrometer at 400 or a Gemini at 300 MHz (¹H) at 96.3 MHz (¹¹B) and 282.4 MHz (¹⁹F) at 298 K; chemical shifts are referenced to the residual protio impurity of the deuterated solvent; IR spectra (nujol mulls, KBr/CsI windows), Perkin–Elmer 577 and 457 grating spectrophotometers.

Electrochemical measurements were carried in out in a standard, three electrode cell with a glassy carbon working electrode, a Pt wire counter electrode and a silver wire pseudo reference electrode. The dichloromethane solution contained 0.1 M tetrabutylammonium hexafluorophosphate as the electrolyte. The concentration of **2a** was 1×10^{-3} M. The solution was sparged with



Fig. 4. EL spectrum of device ITO/α-NPD (50 nm)/2a (50 nm)/LiF (0.5 nm)/Al (100 nm) at 13 V (vertical axis is luminescence; units are arbitrary).

nitrogen prior to each scan and the scans were run with a blanket of nitrogen gas over the top. A scan of the blank solvent was carried out prior to every run. At the completion of the scan, ferrocene was added to a concentration of 1×10^{-3} M and the ferrocene/ferrocenium couple used as an internal reference. Under these conditions the ferrocene $E_{1/2} = 284$ mV, $\Delta E_p = 98$ mV. All potentials in this report are quoted relative to Fc/Fc⁺. All chemicals were obtained commercially and used as received unless stated otherwise.

3.2. Preparation of 3,5-tBu₂-2-(OH)C₆H₂CHN[2-(CO₂H)C₆H₄] (1a)

Formic acid (4 drops) was added to a solution of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (5.12 g, 21.85 mmol) and anthranilic acid (3.00 g, 21.88 mmol) in ethanol (70 cm³). The solution was refluxed for 12 h and concentrated to about 30 cm³ and allowed to evaporate at ambient temperature for 2–3 days to afford **1a** as a vellow solid. Yield 5.30 g. 74%. Further recrystallisation from dimethoxyethane/diethylether (50:50) afforded 1a as a yellow crystalline solid. Anal. Calc. for C₂₂H₂₇NO₃·0.75DME: C, 71.3; H, 8.2; N, 3.3. Found: C, 71.1; H, 8.0; N, 3.7%. Mass Spec. (Nano-electrospray (positive mode), accurate mass measurement): found 354.2072 calculated 354.2064 ([M+H]⁺). IR: 1694w, 1655s, 1612w, 1415w, 1393m, 1364s, 1326w, 1273m, 1251m, 1223m, 1201w, 1169m, 1026w, 964w, 932w, 880w, 829w, 801w, 771m, 738m, 727s, 694w, 644w. ¹H NMR (CDCl₃): δ 1.26 (s, 9H, C(CH₃)₃), 1.36 (s, (H, C(CH₃)₃), 3.34 (s, 3H, OCH₃, 1/2 dme), 3.49 (s, 2H, OCH₂, 1/2 dme), 6.59-7.89 (several m, 7H, arylH+ CH=N), 9.81 (s, 1H, CO₂H), 11.58 (s, 1H, OH).

3.3. Preparation of 3,5-tBu₂-2-(OH)C₆H₂CHN[2-(CO₂H)C₁₀H₆] (**1b**)

As for **1a**, but using 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde (3.76 g, 16.05 mmol) and 3-amino-2-napthoic acid (3.00 g, 16.03 mmol) affording yellow **1b**. Yield 4.90 g, 76%. *Anal.* Calc. for $C_{26}H_{29}NO_3$: C, 77.4; H, 7.2; N, 3.5. Found: C, 77.4; H, 7.1; N, 3.4%. Mass Spec. (ES, positive mode): 404.5 ([M+H]⁺). IR: 1694w, 1655s, 1612w, 1495w, 1415m, 1364s, 1325w, 1273m, 1251m, 1223w, 1201w, 1169m, 1026w, 964w, 932w, 880w, 829w, 801w, 771m, 727s, 694w, 644w. ¹H NMR (CDCl₃): δ 1.35 (s, 9H, C(CH₃)₃), 1.45 (s, (H, C(CH₃)₃), 2.20 (s, 6H, 2MeCN), 7.28–7.61 (several m, 9H, aryl*H*+ *CH*=N), 9.89 (s, 1H, CO₂*H*), 11.66 (s, 1H, O*H*).

3.4. Preparation of $\{3,5-tBu_2-2-(O)C_6H_2CHN[2-(CO_2)C_6H_4]\}B(OMe)\}$ (2a)

To **1a** (2.17 g, mmol) in toluene (30 cm³) was added via syringe B(OMe)₃ (1.6 cm³, mmol) and the system was refluxed for 12 h. Following removal of volatiles *in-vacuo*, the residue was extracted into warm MeCN. Prolonged standing at ambient temperature afforded **2a** as large yellow prisms. Yield 2.03 g, 59%. *Anal.* Calc. for C₂₃H₂₈BNO₄: C, 70.2; H, 7.2; N, 3.6. Found: C, 69.6; H, 7.1; N, 4.0%. ¹H NMR (CDCl₃): δ 1.34 (s, 9H, C(CH₃)₃), 1.52 (s, (H, C(CH₃)₃), 2.02 (s, 3H, CH₃CN), 3.26 (s, 3H, OCH₃), 7.28–8.33 (several m, 6H, aryl*H*), 8.80 (s, 1H, C*H*=N). ¹¹B NMR (CDCl₃) δ 5.53 s. IR (powdered sample) ν /cm⁻¹: 2956 (m), 1739 (m), 1694 (m), 1611 (m), 1553 (w), 1506 (w), 1474 (s), 1392 (m), 1365 (vs), 1336 (m), 1307 (s), 1239 (m), 1202 (m), 1102 (s), 1071 (m), 1040 (m), 1019 (m), 878 (w), 796 (w), 758 (s), 750 (s), 693 (m), 681 (w). UV–Vis (MeOH) λ /nm (relative absorbances): 223 (0.78), 258 (0.23), 325 (0.32), 400 (0.15). Emission max (CH₂Cl₂): λ 385 nm.

3.5. Preparation of {[3,5-tBu₂-2-(0)C₆H₂CHN[2-(CO₂)C₁₀H₆]]]B(OMe)} (**2b**)

As for **2a**, but using **1b** (2.0 g, 4.96 mmol) and $B(OMe)_3$ (1.2 cm³, 10.5 mmol) affording **2b** 2MeCN as yellow prisms. Yield 1.06 g,

48%. *Anal.* Calc. for C₂₇H₃₀BNO₄·2MeCN: C, 70.9; H, 6.9; N, 8.0. Found: C, 70.2; H, 6.7; N, 7.1%. Mass Spec. (EI): 443.3 ([M]⁺), 412.3 ([M]⁺–OMe). IR: 2361w, 1700w, 1624w, 1610w, 1547w, 1305bw, 1260s, 1202bw, 1096bs, 1020bs, 880w, 794s, 723s, 695w, 666w. ¹H NMR (CDCl₃): δ 1.34 (s, 9H, C(CH₃)₃), 1.51 (s, (H, C(CH₃)₃), 2.00 (s, 3H, CH₃CN), 3.24 (s, 3H, OCH₃), 7.39 (d, 1H, arylH), 7.58 (m, 2H, arylH), 7.76 (d, 1H, arylH), 7.90 (m, 2H, arylH), 8.07 (s, 1H, arylH), 8.79 (s, 1H, arylH), 8.91 (s, 1H, CH=N). ¹¹B NMR (CDCl₃) δ 5.73s. UV–Vis (CH₂Cl₂) λ /nm (relative absorbances): 230 (0.48), 273 (0.14), 300 (0.19), 334 (010), 419 (0.09). Emission max (CH₂Cl₂): λ 445 nm.

3.6. Preparation of [{3,5-tBu₂-2-(0)C₆H₂CHN[2-(CO₂)C₆H₄]}B(thf)][CF₃SO₃]) (**3a**)

To a solution of **2a** (1.00 g, 2.54 mmol) in toluene (20 cm³) was added a solution of trifluoromethanesulfonic acid (0.23 cm³, 2.60 mmol) in toluene (10 cm³) at ambient temperature. After stirring for 12 h, volatiles were removed *in-vacuo* and the yellow residue was extracted into THF (30 cm³). Yield: 1.14 g, 77%. *Anal.* Calc. for C₂₇H₃₂BSF₃NO₇: C, 55.7; H, 5.5; N, 2.4. Found: C, 55.7; H, 5.5; N, 2.4%. IR: 1610w, 1552w, 1288w, 1260m, 1225w, 1192bw, 1096bs, 1015bs, 960w, 805m, 723w, 662w. ¹H NMR (C₆D₆) δ 9.28 (s, 1H, CH), 7.77, 7.11, 6.99 (3x bm, 6H, aryl*H*), 3.35 (s, 4H, OCH₂), 1.41 (s, 4H, CH₂), 1.31 (s, 9H, C(CH₃)₃), 1.10 (s, 9H, C(CH₃)₃). ¹¹B NMR (C₆D₆) δ 2.90. ¹⁹F NMR (C₆D₆) δ –77.87. UV–Vis (CH₂Cl₂) λ /nm (relative absorbances): 235 (0.42), 258 (0.09), 332 (0.38), 418 (0.11). Emission max (CH₂Cl₂): λ 385 nm.

3.7. Preparation of [{3,5-tBu₂-2-(0)C₆H₂CHN[2-(CO₂)C₁₀H₆]}B(thf)][CF₃SO₃]) (**3b**)

As for **3a**, but using **2b** (1.00 g, 2.26 mmol) and trifluoromethanesulfonic acid (0.20 cm³, 2.26 mmol). Yield: 0.87 g, 61%. *Anal.* Calc. for $C_{31}H_{34}BSF_{3}NO_7$: C, 58.9; H, 5.4; N, 2.2. Found: C, 58.8; H, 5.5; N, 2.1%. IR: 1590w, 1280bm, 1255s, 1091bs, 1015bs, 866w, 794s, 723s, 690w. ¹H NMR (C₆D₆) δ 9.21 (s, 1H, CH), 8.98, 8.85, 7.78, 7.47 (4x bm, 8H, arylH), 3.35 (s, 4H, OCH₂), 1.44 (s, 4H, CH₂), 1.27 (s, 9H, C(CH₃)₃), 1.12 (s, 9H, C(CH₃)₃). ¹¹B NMR (C₆D₆) δ 3.23. ¹⁹F NMR (C₆D₆) δ –77.82. UV–Vis (CH₂Cl₂) λ /nm (relative absorbances): 233 (0.52), 261 (0.38), 347 (0.10). Emission max (CH₂Cl₂): λ 383 nm.

3.8. Fabrication of electroluminescent device

The EL device using **2a** as the emitting layer and electron transport layer was fabricated on indium tin oxide (ITO). The ITO was cleaned by successive 20 min sonications in neutral detergent, 1:1 NH₃/H₂O₂ and then deionised water. Between each sonication the substrates were rinsed with deionised water. The substrates were dried in an oven at 120 °C for 1 h and then subjected to an oxygen plasma clean. The device was prepared by evaporation from molybdenum crucibles at pressures below 1×10^{-6} mbar. The thickness of the layers was calibrated using a Dektak profilometer. The structure of the device fabricated was: ITO/ α -NPD (50 nm)/**2a** (50 nm)/LiF (0.5 nm)/Al (100 nm), where α -NPD is *N*,*N*'-diphenyl-*N*,*N*'-bis(1-naphthyl)-1-1'-biphenyl-4,4'-diamine. The devices were tested under vacuum.

3.9. X-ray crystallography

Measurements for **1a** and **2b**·2MeCN were made on a Bruker AXS SMART 1000 CCD diffractometer equipped with graphite monochromated Mo K α radiation. Narrow-frame exposures (0.3° in ω) were employed. Cell parameters were refined from all strong reflections in each data set. Intensities were corrected semi-empirically for absorption, based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full-matrix-least squares on F^2 values for all unique data. All non-hydrogen atoms were refined anisotropically. H atoms were included in a riding model with U_{iso} set to be 1.2 times (1.5 times for methyl-H) U_{eq} for the carrier atom. Further details are presented in Table 3. In **1a** the diffraction data were twinned via a rotation of 180° about $[\bar{1}00]$ in direct space with a major:minor component ratio of 61.51:38.49(4)%. Modeling the twinning resulted in a substantial improvement in the structure refinement. In 2b-2MeCN one tBu group and both molecules of MeCN showed some signs of disorder but were modeled as a single set of atomic positions, refined with restraints on displacement parameters. Programs used were Bruker AXS SHELXTL [11] for structure solution, refinement, and molecular graphics, Bruker AXS SMART (control) and SAINT (integration) [12], and local programs.

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Appendix A. Supplementary material

CCDC 705300 and 705301 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2009.11.006.

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