SHORT PAPER

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Synthesis and characterisation of dibenzofuran derivatives[†]

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A series of arylamine derivatives of dibenzofuran were synthesised and the X-ray structure of compound **2**, 4,6-diformylbenzofuranbis(2,6-diisopropylanil), was solved.

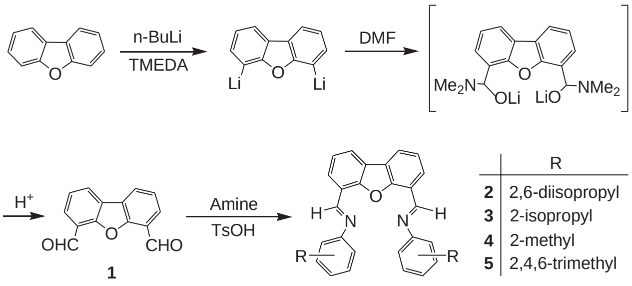
Keywords: dibenzofuran, derivatives, lithiation

In the exploration of late-metal complexes for ethylene polymerisation, much effort has been put on the design and synthesis of ligands with large steric bulk. Impressive examples are the α-diimine ligands and the bis(imino)pyridyl ligands.[1-3] Variation of the bulkiness of the ligands leads to products from polyolefins to oligomers.[4-7] Dibenzofuran, like its analogue xanthene, possesses two large flat rings and can undergo lithiation readily in its 4- and 6-positions. It allows for the design and synthesis of specially shaped molecules with rigidity and a large bite angle. These are good candidates for the study of molecular recognition,[8,9] catalytic reactions[10,11] and the geometry of metal-binding sites.[12–14] Dibenzofuran was chosen as the backbone in constructing molecules with large bulkiness. Here we report the syntheses and characterisations of some imino-derivatives of dibenzofuran and the X-ray analysis of compound **2**.

The dicarboxaldehyde was synthesised according to the literature.[11] The lithiation of dibenzofuran was carried out in an ice-bath, and the mixture was stirred at room temperature for several hours in order to complete the reaction. The condensation reaction of the dicarboxaldehyde and an arylamine was easily performed (Scheme 1). The purification of the products sometimes seemed difficult because of the residual with unreacted arylamine, but fortunately the final separation could be accomplished by using Kugelrohr distillation and column chromatography.

The resulting products **2–5** were fully characterised by their melting point, IR spectra, ^{1}H NMR spectra, EA, and MS. In their IR spectra, bands in the range 1626–1639 cm^{-1} are ascribed to the stretching vibration of C=N. In ^{1}H NMR spectra, the signal of the CH=N is in the range 8.82–9.07 ppm, while the signal of the CHO of the dialdehyde is at 10.72 ppm. Unfortunately, the preparation of late-metal complexes of compounds **2–5** was not successful. A stable nickel (II) complex with bis(oxazoline)dibenzofuran ligand has been reported recently.[10] The difference between bis(oxazoline)dibenzofuran and compound **2** is that the nitrogen atoms of the former are constrained to a *cis, cis* conformation by the rigid oxazoline rings. In the current case, the coordination ability of the oxygen atom of the dibenzofuran is weak and coordination of imino group is unfavourable to late-metals.

To clarify the structure of the synthesised compounds, single crystals of compound **2** suitable for X-ray analysis were obtained by slow evaporation of an ethanol solution of the compound. The structure of compound **2** is shown in Fig. 1. Its selected bond lengths and angels are collected in Table 1. The bond lengths of N(1)–C(7) and N(2)–C(27) are 1.256(3) and 1.262(3) Å, respectively. The bond angles of C(7)–N(1)–C(8) and C(27)–N(2)–C(28) are 117.9(2) and 116.4(2)°, close to 120°. The two aryl rings take an *E, E* conformation according to the C=N bond.[15] They are nearly perpendicular to the plane of dibenzofuran with the dihedral angles of 93.7° and 113.4°, respectively. The two aryl rings are not parallel to each other, with a dihedral angle of 23.8°. There is a weak intermolecular π–π interaction between the neighboring dibenzofuran planes which



	R
2	2,6-diisopropyl
3	2-isopropyl
4	2-methyl
5	2,4,6-trimethyl

Scheme 1 The synthesis of dibenzofuran derivatives **2–5**.

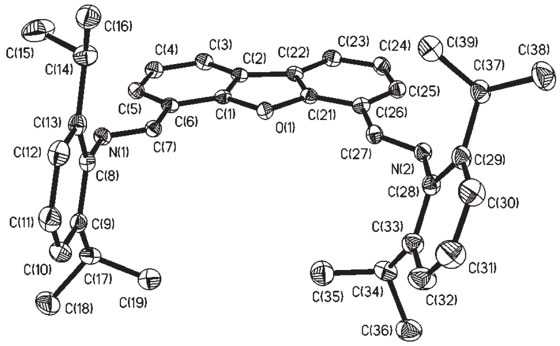


Fig. 1 Molecular structure of compound **2** showing 30% probability displacement ellipsoids with hydrogen atoms omitted for clarity.

Table 1 Selected bond lengths [Å] and angles [°] for compound **2**

Bond length [Å]			
O(1)–C(1)	1.375(3)	O(1)–C(21)	1.384(3)
N(1)–C(7)	1.256(3)	N(1)–C(8)	1.429(3)
N(2)–C(27)	1.262(3)	N(2)–C(28)	1.431(3)
Bond angle [°]			
C(1)–O(1)–C(21)	104.99(17)	C(7)–N(1)–C(8)	117.9(2)
C(27)–N(2)–C(28)	116.4(2)	O(1)–C(1)–C(2)	112.3(2)
O(1)–C(1)–C(6)	123.2(2)	N(1)–C(7)–C(6)	122.5(2)
O(1)–C(21)–C(26)	123.1(2)	O(1)–C(21)–C(22)	111.9(2)
N(2)–C(27)–C(26)	123.4(2)		

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

is similar to the reported complexes.[16] The centroid–centroid distance of the parallel planes (O1–C1–C2–C22–C21 and C1A–C2A–C3A–C4A–C5A–C6A, where A donates the symmetry operator: 1–*x*, 1–*y*, 1–*z*) is 3.636 Å.

Experimental

All manipulations of moisture-sensitive compounds were carried out under an atmosphere of nitrogen using standard Schlenk techniques. Melting points (m.p.) were determined with a digital electrothermal apparatus without calibration. The IR spectra were obtained on a Perkin-Elmer FT-IR 2000 spectrophotometer by using the KBr disc in the range of 4000–400 cm^{-1}. The ^1H NMR spectra were recorded on a Varian Unity 200 instrument with TMS as the internal standard. Splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; hept, heptet; m, multiplet. Elemental analyses were performed on a Flash EA 1112 microanalyzer. MS was performed on an AEI MS-50 spectrometer. Solvents were refluxed over an appropriate drying agent and distilled under nitrogen prior to use. All other chemicals were obtained commercially and used without further purification unless stated otherwise.

4,6-Dibenzofurandicarbaldehyde **1**: Dibenzofuran (2.52 g, 15 mmol) was dissolved in dry hexane (50 ml) containing N,N,N',N'-tetramethylethylenediamine (6.8 ml, 45 mmol). To this solution was added *n*-butyllithium (1.3 M in hexane, 15.0 ml, 19.5 mmol) and the mixture was stirred under nitrogen for 5 h. DMF (3.5 ml, 45 mmol) was added over 10 minutes with cooling on ice, and the mixture was stirred at room temperature for 12 hr. It was then poured into HCl solution (1 M, 300 ml). The water phase was extracted several times with dichloromethane, in total about 100 ml. The combined organic phase was dried over $MgSO_4$ and the solvent was evaporated. The crude product was purified by recrystallisation from hot methanol affording a yellow powder (1.90 g, 57% yield), m.p. 220–222 °C. ^1H NMR (200 MHz, $CDCl_3$/ppm): δ 7.57–8.28 (m, 6H, ArH), 10.72 (s, 2H, CHO).

4,6-Diformylbenzofuranbis(2,6-diisopropylanil) **2**: **1** (224 mg, 1 mmol) and 2,6-diisopropylaniline (531 mg, 3 mmol) were dissolved in ethanol (30 ml). *p*-Toluenesulfonic acid (ca. 10 mg) was added and the solution was refluxed for 12 h. The ethanol was removed in vacuum. The crude product was purified by chromatography on an alumina column elution with petroleum ether / ethyl acetate 19:1 and Kugelrohr distillation affording a yellow solid (0.40 g, 74% yield), m.p. 180–182 °C. Anal. Calc. for $C_{38}H_{42}N_2O$ (542.75): C, 84.09; H, 7.80; N, 5.16. Found: C, 84.04; H, 7.79; N, 5.15. ^1H NMR (200 MHz, $CDCl_3$/ppm): δ 1.13 (s, 12H, CH_3), 1.16 (s, 12H, CH_3), 2.99 (hept, 4H, CH), 7.13–8.34 (m, 12H, ArH), 8.82 (s, 2H, CHN). Positive EI-MS: ion at *m/e* 542 {M^+}. IR (KBr disc, cm^{-1}): 2961 (s), 1639 (s), 1461 (m), 1433 (m), 1181 (s), 779 (m), 749 (m). Compounds **3**–**5** were prepared analogously from **1** and the corresponding arylamines.

4,6-Diformylbenzofuranbis(2-isopropylanil) **3**: A yellow solid (0.21 g, 46% yield), m.p. 124–126 °C. Anal. Calc. for $C_{32}H_{30}N_2O$ (458.59): C, 83.81; H, 6.59; N, 6.11. Found: C, 83.78; H, 6.60; N, 6.22. ^1H NMR (200 MHz, $CDCl_3$/ppm): δ 1.23 (s, 6H, CH_3), 1.26 (s, 6H, CH_3), 3.61 (hept, 2H, CH), 7.01–8.30 (m, 14H, ArH), 9.07 (s, 2H, CHN). IR (KBr disc, cm^{-1}): 2959 (s), 1626 (s), 1481 (m), 1429 (m), 1411 (m), 1180 (s), 775 (m), 752 (s).

4,6-Diformylbenzofuranbis(2-methylanil) **4**: A yellow solid (0.31 g, 73% yield), m.p. 164–166°C. Anal. Calc. for $C_{28}H_{22}N_2O$ (402.49): C, 83.56; H, 5.51; N, 6.96. Found: C, 83.14; H, 5.54; N, 6.73. ^1H NMR (200 MHz, $CDCl_3$/ppm): δ 2.45 (s, 6H, CH_3), 7.09–8.31 (m, 14H, ArH), 9.07 (s, 2H, CHN). IR (KBr disc, cm^{-1}): 2904 (w), 1629 (s), 1484 (m), 1429 (m), 1412 (m), 1182 (s), 774 (m), 737 (s).

4,6-Diformylbenzofuranbis(2,4,6-trimethylanil) **5**: A yellow solid (0.31 g, 68% yield), m.p. 212–214 °C. Anal. Calc. for $C_{32}H_{30}N_2O \cdot H_2O$ (476.26): C, 80.64; H, 6.77; N, 5.88. Found: C, 80.68; H, 6.41; N, 5.82. ^1H NMR (200 MHz, $CDCl_3$/ppm): δ 2.15 (s, 12H, CH_3), 2.28 (s, 6H, CH_3), 6.89–8.33 (m, 14H, ArH), 8.85 (s, 2H, CHN). IR (KBr disc, cm^{-1}): 2913 (m), 1639 (s), 1478 (m), 1430 (m), 1407 (m), 1203 (m), 1183 (s), 850 (m), 778 (m), 743 (m).

X-ray crystal structure determination of compound **2**: Intensity data sets of compound **2** were collected at 293 K on a Rigaku RAXIS RAPID IP diffractometer with graphite-monochromated MoKα (λ = 0.71073 Å) radiation, using the ω oscillation. Cell parameters were obtained by the global refinement of the positions of all collected reflections. $C_{38}H_{42}N_2O$, *Mr* = 542.75, triclinic, P-1, *a* = 13.4263(4) Å, *b* = 14.2964(10) Å, *c* = 8.4860(3) Å, α = 95.440(3)°, β = 105.183(2)°, γ = 78.230(3)°, *V* = 1537.4(6) $Å^3$, *D* = 1.172 g cm^{-3}, *Z* = 2, μ = 0.070 mm^{-1}, *T* = 296(2) K. Intensity data sets were corrected for Lorentz and polarisation effects and empirical absorptions were applied by using ABSCOR program. The structure was solved by direct methods. The final refinement was done by full-matrix least-squares on F^2 methods with anisotropic thermal parameters for non-hydrogen atoms and isotropic thermal parameters for geometric hydrogen atoms by using SHELX-97 package[17]. Non-hydrogen atoms were subjected to anisotropic refinement. The final refinement was converged at *R* = 0.0555, *wR* = 0.1266 for 3116 observed reflections with $I > 2\sigma(I)$. Full crystallographic details were deposited at the Cambridge Crystallographic Data Centre with CCDC number 218195.

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