Unexpected Formation and Crystal Structure of a Spiro[indene-1,7'(6'*H*)-pyrrolo[3,4-*b*]pyridin]-5'-one

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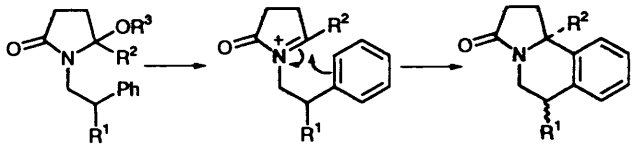
Dehydration of 6,7-dihydro-7-hydroxy-6-(α-methylbenzyl)-7-phenylpyrrolo[3,4-*b*]pyridin-5-one **4b** on treatment with acid is accompanied by rearrangement, first to 6,7-dihydro-7-phenyl-7-[(*E*)-2-phenylethenyl]pyrrolo[3,4-*b*]pyridin-5-one **10** and then to 2,3-dihydro-3-phenylspiro[indene-1,7'(6'*H*)-pyrrolo[3,4-*b*]pyridin]-5'-ones **9a**, **b**. Crystal structures of two rearranged products **9a** and **10** are reported.

The stereoselectivity of *N*-acyl iminium ion cyclisations is usually attributed to kinetic control, the result of stereoelectronic influences in the transition state.[1] Of particular relevance to our own work are studies by Maryanoff and coworkers,[2] in which the diastereoselectivity of tricyclic products **2** formed from hydroxy lactams **1a** or lactam ethers **1b** in polyphosphoric acid (PPA) has been interpreted in terms of the steric requirements of the substituent R^1 (Scheme 1). The

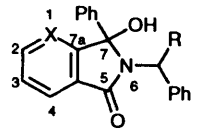


1a R^2 = Me, R^3 = H
b R^2 = H, R^3 = Et

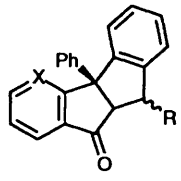
2

Scheme 1

cyclodehydration of hydroxy lactams **3a**, **b** in PPA gives the fused tetracyclic products **5a**, **b**.[3,4] These 5-*endo*-*trig* cyclisations involving the *N*-benzyl group of an intermediate *N*-acyl



3a X = CH, R = H
b X = N, R = H
4a X = CH, R = Me
b X = N, R = Me

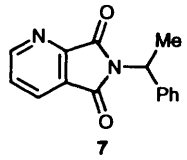


5a X = CH, R = H
b X = N, R = H
6a X = CH, R = Me
b X = N, R = Me

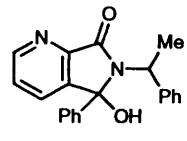
iminium ion are achieved only when an aryl group is present on the iminium carbon atom. For cyclodehydration of the *N*-α-methylbenzyl compounds **4a**, **b**, it seemed that the corresponding products **6a**, **b** might be more easily formed with the Me, Ph groups *cis* rather than *trans*, because in the latter case the methyl group must lie on the more crowded side of the 5,5-bicyclic system. In attempting to test this prediction, we observed an unexpected rearrangement resulting in the formation of novel spiro structures.

Results and Discussion

Hydroxy lactam **4b** was the major product of phenyl Grignard addition to the pyridine-2,3-dicarboximide **7**; ^1H and ^{13}C NMR spectra showed that two diastereoisomers of **4b** were present in similar amounts. A by-product, the regioisomeric hydroxy lactam **8**, was recognised by the chemical shift of the



7

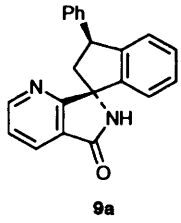


8

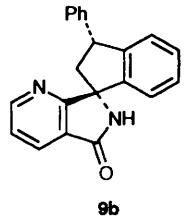
resonance for C-7a (δ 151.9) in comparison with the more deshielded C-7a resonance in **4b** (δ 165.0 or 165.8, the other being due to C-5 of the carbonyl group).[4]

Heating the hydroxy lactam **4b** in PPA at 100–125 °C resulted in the formation of two products (3:1 ratio, 58% yield), both $C_{21}H_{16}N_2O$, consistent with our expectation of cyclisation to structure **6b**. That these are two diastereoisomers was shown by the very close similarities between them in respect to all significant features of IR, NMR and mass spectra. The same two products were obtained in the same ratio starting from a single diastereoisomer of **4b** or from a mixture of its diastereoisomers, as expected if the first step involves formation of a planar *N*-acyl iminium ion intermediate. However, the absence of a methyl group (^1H and ^{13}C NMR spectra) and the presence of NH (IR and ^1H NMR spectra) attached to CO (IR and ^{13}C NMR spectra) clearly rule out structure **6b**. The ^1H NMR spectra at 300 MHz include an ABX pattern, for which the coupling constants [J_{AB} 13.5 (13.2), J_{AX} 7.3 (7.6), J_{BX} 9.8 (9.4) Hz for the major (minor) compounds, respectively] are appropriate to CH_2CH in a five-membered ring. These assignments were confirmed by appropriate selective NMR decoupling experiments and by a 2-D NOESY spectrum. The corresponding ^{13}C NMR signals were present at δ 48.4 (47.9) and 50.1 (48.7) for CH_2CH, respectively, and a quaternary carbon resonance at δ 73.0 (71.6).

As several structures could be considered to account for this feature and for the other spectroscopic evidence, the problem was solved by X-ray crystallography which proved the spiro



9a



9b

lactam structure **9a** for the major product (Fig. 1). The crystal structure of **9a** contains an unusually elongated unit cell, in which enantiomeric pairs of molecules are held together by C=O · · · H–N hydrogen bonds (N–O interatomic distance 2.84 Å). The minor diastereoisomer is therefore **9b**.

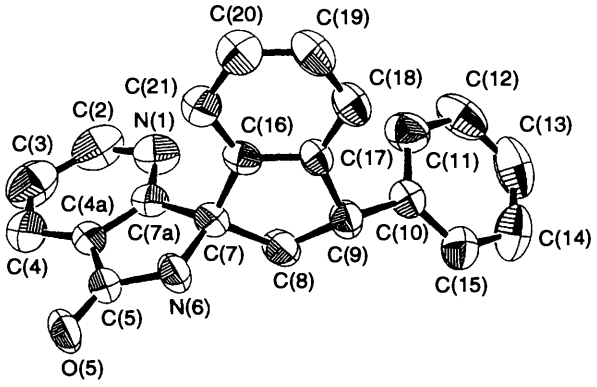


Fig. 1 ORTEP drawing of the structure of compound **9a** with crystallographic numbering scheme (hydrogen atoms omitted)

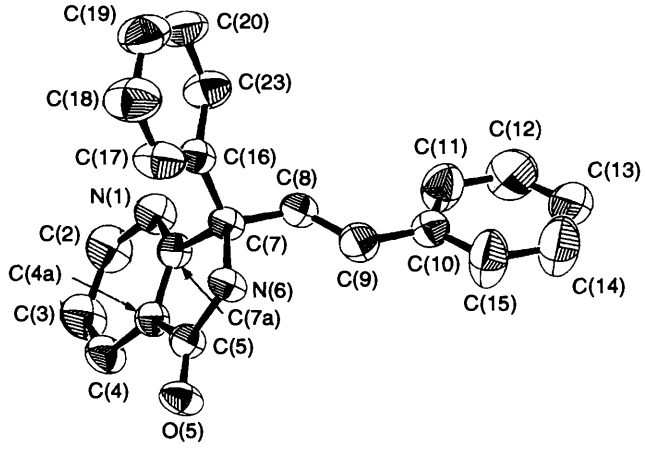
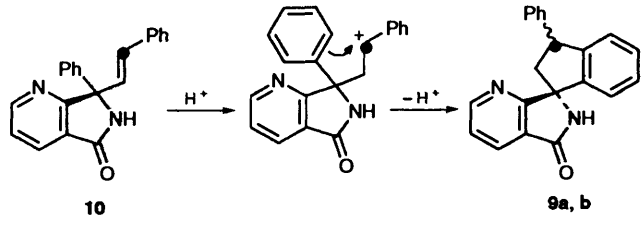


Fig. 2 ORTEP drawing of the structure of compound **10** with crystallographic numbering scheme (hydrogen atoms omitted)

Heating the same hydroxy lactam **4b** in refluxing trifluoroacetic acid (TFA) gave a third product, isomeric with **9a**, **b**, which was converted into **9a**, **b** in the same 3:1 ratio by heating in PPA, as for **4b**. This new product also contains the NHCO grouping (IR and NMR absorptions) and a *trans*-disubstituted alkene (δ_H 6.78 and 6.92, two doublets, J 16.1 Hz), observations which suggested structure **10**. A 2-D ^1H–^{13}C NMR correlation spectrum showed that the ^1H resonance at higher field belonged with the ^{13}C resonance at δ 130.3 and the ^1H resonance at lower field with the ^{13}C resonance at δ 128.8, which is consistent with a β-substituted styrene.[5] Structure **10** was also confirmed by single crystal X-ray diffraction (Fig. 2). Recognition of **10** as an intermediate allows us to account for the formation of **9a**, **b** in terms of the mechanism shown in Scheme 2.



10 **9a, b**

Scheme 2 (● denotes ^{13}C label)

Isotopic labelling experiments provided additional information concerning the nature of the rearrangement involved in the formation of **10** and **9**. Compound **4b** containing ^{13}C at the benzylic *N*-CH position was prepared in three steps starting from ^{13}CO-labelled acetophenone. Samples of **9a**, **b** were then prepared, in a single step from **4b** in PPA and in two steps *via* **10**. In both cases, the ^{13}C label was located only at the PhCH carbon in both **9a** and **9b**, as shown in Scheme 2. In the styrene derivative **10**, the ^{13}C NMR signal at δ 130.3 was enhanced due to the ^{13}C enrichment, and the ^1H NMR doublet at δ 6.78 showed satellite lines due to ^{13}C–^1H coupling, proving that the labelled alkene carbon is that attached to the phenyl group.

It follows that the methyl group in compound **4b** is the source of the ring CH_2 group in **9a**, **b**, which we have also confirmed by deuterium-labelling experiments. No migration of a phenyl group is involved. And in contrast to the reactions **3a**, **b**→**5a**, **b**, where the *N*-benzyl group is involved in the cyclisation, it is the 7-phenyl group in **4b** which becomes incorporated into the spiro indene structure **9**. Other aspects of this reaction are the subject of further investigation.

Experimental

IR Spectra were recorded for Nujol mulls and calibrated with polystyrene (Pye Unicam SP3-200). ^1H NMR Spectra were recorded at 90 (JEOL-JNM-FX90Q) or 300 MHz (Bruker MSL300) and ^{13}C NMR spectra at 22.5 or 75 MHz (on the same instruments) for solutions in [^2H]chloroform with tetramethylsilane as internal standard. J Values are given in Hz. Mass spectra were obtained by electron impact at 70 eV (Kratos MS30 and VG Autospec). Chromatography was performed on MN-silica gel 60. Diethyl ether and tetrahydrofuran (THF) were dried before use. Light petroleum refers to the fraction, b.p. 40–60 °C.

N-α-Methylbenzylpyridine-2,3-dicarboximide **7** was prepared by the method described in ref. 4 from pyridine-2,3-dicarboxylic acid and racemic α-methylbenzylamine; m.p. 90.5–92 °C (from toluene–light petroleum); ν_{max}/cm^{-1} 1740 and 1715 (CO) (Found: M^+ 252.089 84. Calc. for $C_{15}H_{12}N_2O_2$: M^+, 252.089 87). Another sample prepared from (*S*)-(−)-α-methylbenzylamine had m.p. 119–120 °C (from ethanol) but identical IR, NMR and mass spectra.

6,7-Dihydro-7-hydroxy-6-(α-methylbenzyl)-7-phenylpyrrolo-[3,4-b]*pyridin-5-one* **4b**.—The Grignard reagent was prepared from bromobenzene (2.5 g, 16 mmol) and magnesium (0.39 g) in THF (25 cm^3). This solution was cooled in ice and stirred during rapid addition of the *N*-α-methylbenzyl imide **7** (1.0 g, 4.0 mmol) in THF (25 ml) and for a further 3 h. The mixture was poured into saturated aqueous ammonium chloride (200 cm^3) and the product extracted into chloroform (3 × 20 cm^3). The combined extracts were washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was chromatographed on silica eluting with chloroform–ethyl acetate (4:1 v/v) to give the hydroxy lactam **4b** as a *ca.* 1:1 mixture of diastereoisomers (1.00 g, 76%) (from toluene–light petroleum). Fractional crystallisation from toluene–light petroleum achieved partial separation and gave material, m.p. 165–167 °C; ν_{max}/cm^{-1} 3350 (OH) and 1690 (CO); δ_H 1.65 and 1.79 (3 H, 2 d, J 7.1, Me of two diastereoisomers), 4.4–4.9 (1 H, 2 overlapping q, methine CH), 7.09–7.60 (12 H, m, phenyl, OH and 3-H), 7.97 (1 H, dd, 4-H) and 8.20 (1 H, dd, 2-H); δ_C 18.4 and 19.3 (2 q, Me of two diastereoisomers), 52.2 (d, methine CH), 91.2 and 92.0 (2 s, C-7 of two diastereoisomers), 124.4, 125.7, 126.3, 127.2, 127.8, 128.2, 128.7, 128.9, 131.9, 137.2, 141.5, 142.2, 152.3, 165.0 and 165.8; m/z 315 (M − Me, 1%), 210 (36), 120 (100), 105 (26) and 77 (24).

In a subsequent experiment, product separation by column chromatography gave in early fractions 5,6-dihydro-5-hydroxy-6-(α-methylbenzyl)-5-phenylpyrrolo[3,4-*b*]pyridin-7-one **8** (61 mg, 4.6%), m.p. 110–112 °C (from toluene–light petroleum); δ_H 1.72 (3 H, overlapping d, J 7.2, Me of two diastereoisomers), 2.35 (1 H, s, OH), 4.55–4.99 (1 H, overlapping q, methine CH for two diastereoisomers), 7.11–7.66 (12 H, m, phenyl, 3-H and

4-H) and 8.29 (1 H, d, *J* 5.3, 2-H); δ_C 19.6 (q, Me), 52.6 (d, methine CH), 90.5 (s, C-5), 121.4, 125.3, 125.5, 126.7, 126.9, 127.8, 128.0, 128.2, 128.6, 129.0, 129.7, 134.4, 137.9, 141.8, 149.3, 151.9 and 164.9.

2,3-*Dihydro*-3-*phenylspiro*[*indene*-1,7'(6'H)-*pyrrolo*[3,4-b]-*pyridin*]-5'-*ones* **9a**, **b**.—The hydroxy lactam **4b** (403 mg, 1.22 mmol) was dissolved in PPA (32 g) and heated at 120–125 °C for 1 h. The hot solution was poured onto crushed ice, thoroughly stirred, and extracted with chloroform (3 × 20 cm^3). The organic extract was washed with water, dried ($MgSO_4$), and evaporated to dryness. The residue was chromatographed on silica eluting the column with chloroform–ethyl acetate (4:1 v/v) to give the spiro indene **9b** (52 mg, 13%), m.p. 215–217 °C (from toluene–light petroleum) (Found: M^+ 312.126 26. $C_{21}H_{16}N_2O$ requires M^+, 312.126 26); δ_H 2.58 (1 H, dd, *J* 9.4 and 13.2) and 3.06 (1 H, dd, *J* 7.6 and 13.2, CH_2), 4.99 (1 H, overlapping dd, 3-H), 6.96–7.44 (11 H, m, phenyl, 3'-H and NH), 8.12 (1 H, dd, *J* 1.5 and 7.6, 4'-H) and 8.65 (1 H, dd, *J* 1.5 and 4.5, 2'-H); δ_C 47.9 (t, C-2), 48.7 (d, C-3), 71.6 (s, spiro C), 122.6, 123.4, 126.0, 126.9, 127.6, 128.3, 128.8, 129.3, 132.3, 141.9, 146.9, 153.5, 168.3 and 170.3; *m/z* 312 (M^+, 100%), 297 (87), 284 (35), 91 (48), 84 (38) and 49 (55).

Further elution gave the spiro indene **9a** (163 mg, 43%), m.p. 209–211 °C (from toluene–light petroleum) (Found: C, 80.6; H, 5.1; N, 8.9. $C_{21}H_{16}N_2O$ requires C, 80.7; H, 5.2; N, 9.0%); ν_{max}/cm^{-1} 3200w (NH) and 1720s (CO); δ_H 2.75 (1 H, dd, *J* 7.3 and 13.5) and 3.09 (1 H, dd, *J* 9.8 and 13.5, CH_2), 4.76 (1 H, overlapping dd, 3-H), 6.67–7.44 (10 H, m, phenyl and 3'-H), 7.94 (1 H, s, NH), 8.15 (1 H, dd, *J* 1.5 and 7.6, 4'-H) and 8.77 (1 H, dd, *J* 1.5 and 4.7, 2'-H); δ_C 48.4 (t, C-2), 50.1 (d, C-3), 73.0 (s, spiro C), 124.1, 126.1, 126.2, 127.6, 128.5, 129.1, 129.3, 130.0, 132.5, 142.5, 143.9, 148.6, 154.2, 168.5 and 169.4; *m/z* 312 (M^+, 100%), 297 (39), 221 (71) and 91 (48).

6,7-*Dihydro*-7-*phenyl*-7-[(E)-2-*phenylethenyl*]*pyrrolo*[3,4-b]-*pyridin*-5-*one* **10**.—The hydroxy lactam **4b** (1.0 g) was heated under reflux in TFA (25 cm^3) for 72 h. The solution was cooled and poured into saturated aqueous sodium hydrogen carbonate (200 cm^3); it was then extracted with chloroform (3 × 15 cm^3), the extract was dried ($MgSO_4$) and evaporated to dryness. The residue was chromatographed on silica eluting with chloroform–ethyl acetate (4:1 v/v) to afford the styrene derivative **10** (415 mg, 44%, and a further 205 mg containing some unchanged **4b**), m.p. 227–228 °C (from toluene–light petroleum) (Found: N, 9.0. $C_{21}H_{16}N_2O$ requires N, 9.0%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3200w (NH) and 1710s (CO); δ_H 6.78 and 6.93 (each 1 H, d, *J* 16.1, alkene), 7.04–7.54 (11 H, m, phenyl and 3-H), 7.86 (1 H, br s, NH), 8.18 (1 H, dd, *J* 1.5 and 7.6, 4-H) and 8.72 (1 H, dd, *J* 1.5 and 4.7, 2-H); δ_C 69.1 (s, C-7), 123.5, 124.2, 126.6, 126.8, 128.3, 128.6, 128.9, 129.2, 130.3, 132.7, 136.1, 139.7, 153.2, 168.3 and 168.9; *m/z* 312 (M^+, 100%), 210 (21), 120 (42), 105 (22) and 92 (32).

This product **10** (200 mg) was heated in PPA (17 g) at 125 °C for 1 h. Work-up as before, followed by chromatography afforded the diastereoisomeric spiro lactams, **9a** (103 mg, 51.5%) and **9b** (32 mg, 16%).

^{13}C-*Labelling Experiments*.—Acetophenone (5.0 g) containing 5.0% enrichment of ^{13}CO was used in a Leuckart reaction [6] with ammonium formate to give α-methylbenzylamine (2.0 g, 40%), b.p. 80–81 °C/18 mmHg. This amine was then used to prepare ^{13}C-labelled samples of **7**, **8**, **9a**, **b** (59% yield, the same 1:3 ratio as before) and **10** by the procedures already described; ^{13}C-labelled **10** was also converted into **9a**, **b** (73%) by heating in PPA. The enhanced ^{13}C resonances were as follows: **8** δ 52.2, **9a** δ 50.1, **9b** δ 48.7 and **10** δ 130.3.

Table 1 Bond lengths (Å) for non-hydrogen atoms in **9a** [a,b]

O(5)–C(5)	1.243(5)	C(9)–C(10)	1.529(6)
N(1)–C(2)	1.333(6)	C(9)–C(17)	1.512(6)
N(1)–C(7a)	1.327(5)	C(10)–C(11)	1.377(6)
N(6)–C(5)	1.325(5)	C(10)–C(15)	1.375(6)
N(6)–C(7)	1.469(5)	C(11)–C(12)	1.401(6)
C(2)–C(3)	1.397(7)	C(12)–C(13)	1.365(8)
C(3)–C(4)	1.383(7)	C(13)–C(14)	1.361(7)
C(4)–C(4a)	1.378(6)	C(14)–C(15)	1.383(6)
C(4a)–C(5)	1.483(6)	C(16)–C(17)	1.385(5)
C(4a)–C(7a)	1.375(5)	C(16)–C(21)	1.389(6)
C(7)–C(7a)	1.505(6)	C(17)–C(18)	1.389(6)
C(7)–C(8)	1.553(6)	C(18)–C(19)	1.374(6)
C(7)–C(16)	1.518(6)	C(19)–C(20)	1.378(6)
C(8)–C(9)	1.536(6)	C(20)–C(21)	1.394(6)

[a] Estimated standard deviations in the last significant figure are given in parentheses. [b] Numbering as in Fig. 1.

Table 2 Bond lengths (Å) for non-hydrogen atoms in **10** [a,b]

O(5)–C(5)	1.232(2)	C(9)–C(10)	1.467(3)
N(1)–C(2)	1.345(3)	C(10)–C(11)	1.366(3)
N(1)–C(7a)	1.330(2)	C(10)–C(15)	1.368(3)
N(6)–C(5)	1.343(2)	C(11)–C(12)	1.389(4)
N(6)–C(7)	1.466(2)	C(12)–C(13)	1.348(4)
C(2)–C(3)	1.372(3)	C(13)–C(14)	1.336(4)
C(3)–C(4)	1.376(3)	C(14)–C(15)	1.380(4)
C(4)–C(4a)	1.380(3)	C(16)–C(17)	1.373(3)
C(4a)–C(5)	1.482(2)	C(16)–C(23)	1.379(3)
C(4a)–C(7a)	1.374(2)	C(17)–C(18)	1.389(3)
C(7)–C(7a)	1.524(2)	C(18)–C(19)	1.351(4)
C(7)–C(8)	1.510(3)	C(19)–C(20)	1.353(4)
C(7)–C(16)	1.535(3)	C(20)–C(23)	1.384(3)
C(8)–C(9)	1.309(3)		

[a] Estimated standard deviations in the last significant figure are given in parentheses. [b] Numbering as in Fig. 2.

Crystal Data for Spiro Indene **9a**.—$C_{21}H_{16}N_2O$, M = 312.37. Monoclinic, space group $P2_1/n$ (No. 14), a = 6.721(6), b = 33.896(4), c = 7.697(1) Å, β = 108.89(3)°, V = 1659(1) $Å^3$, $F(000)$ = 656.00, μ(Mo-Kα) = 0.78 cm^{-1}, Z = 4, D_c = 1.250 g cm^{-3}.

Crystal Data for Styrene Derivative **10**.—$C_{21}H_{16}N_2O$, M = 312.37. Triclinic, space group $P\bar{1}$ (No. 2), a = 10.171(1), b = 10.374(1), c = 8.4570(7) Å, α = 92.066(10), β = 99.120(8), γ = 106.17(1)°, V = 843.2(2) $Å^3$, $F(000)$ = 328.00, μ(Mo-Kα) = 0.77 cm^{-1}, Z = 2, D_c = 1.23 g cm^{-3}.

Structure Determination.—Colourless single crystals of spiro indene **9a**, 0.5 × 0.25 × 0.1 mm, and styrene derivative **10**, 0.6 × 0.4 × 0.35 mm, mounted on glass fibres were used for X-ray data collection at 23 ± 1 °C. Intensity measurements were collected on a Rigaku AFC6S four-circle diffractometer with graphite-monochromated Mo-Kα radiation, λ = 0.710 69 Å. Accurate unit cell dimensions and an orientation matrix for data collection were obtained from least-squares refinement of the values of 25 centred reflections for **9a**, or 24 for **10**, in the range 25 < 2θ < 30°. Intensities of 3226 reflections were measured for **9a**, or 3134 for **10**, in the range 5 < 2θ < 50° in a ω–2θ scan mode; of these reflections 2968 were unique (R_{int} = 0.059) for **9a**, or 2955 (R_{int} = 0.015) for **10**; equivalent reflections were merged. The measurement of three standard reflections every 150 reflections showed no sign of decay, and azimuthal scans of several reflections indicated no need for absorption corrections. Lorentz and polarisation corrections were applied in the usual way, and small corrections for secondary extinction were applied (coefficient = 1.342 84 × 10^{-6} for **9a**, 1.759 23 × 10^{-6} for **10**).

The structures were solved by direct methods (SIR88) [7] and

expanded using Fourier techniques.[8] Anisotropic thermal parameters were refined for all non-hydrogen atoms. All hydrogen atoms were located by a difference-Fourier map and included but not refined. The final cycle of full matrix least-squares refinement* used 1678 independent reflections for **9a**, or 2346 for **10**, with $I > 3\sigma(I)$ and 218 variable parameters and converged with $R = 0.062$ and $R_w = 0.053$ for **9a**, $R = 0.041$ and $R_w = 0.037$ for **10**. The standard deviation of an observation of unit weight† was 3.84 for **9a**, or 2.98 for **10**. σ-Weights were applied, in which the weight assigned to each observation is equal to the reciprocal of the variance of that observation, $1/\sigma^2(F_{obs})$ for F refinement. This weighting scheme is based on counting statistics and included a factor ($p = 0.005$ for **9a**, 0.010 for **10**) to downweight the intense reflections. Neutral atom scattering factors,[9] mass attenuation coefficients, and the values for dispersion corrections were taken from appropriate International Tables;[10] anomalous dispersion effects were included in F_{calc}.[11] All calculations were performed using the TEXSAN crystallographic software.[12]

Selected bond lengths for **9a** and **10a** are given in Table 1 and Table 2, respectively. The complete listings of fractional atomic coordinates, bond lengths, bond angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallography Data Centre.‡

* The function minimised was $\Sigma\omega(|F_o| - |F_c|)^2$ where $\omega = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/L_p^2$ and S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, L_p = Lorentz-polarisation factor, B = total background count and p = p-factor.

† Standard deviation of an observation of unit weight = $\sqrt{\Sigma\omega(|F_o| - |F_c|)^2/(N_o - N_v)}$ where N_o = number of observations and N_v = number of variables.

‡ For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, issue 1.

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