NJC

Cite this: *New J. Chem.*, 2011, **35**, 2483–2487

www.rsc.org/njc

PAPER

Synthesis of a class of 5-((5-(pyrrol-2-yl-methylene)-pyrrol-2-yl)methylene)-furan-2-ones and the formation of a furanone dipyrrin imino ether†

Ji-Young Shin[ab] **and David Dolphin***[a]

Received (in Gainesville, FL, USA) 12th May 2011, Accepted 17th July 2011
DOI: 10.1039/c1nj20415g

A class of α-furanyl dipyrrins **2** were prepared by refluxing THF solutions of DDQ adducts **1** with the appropriate alcohols in the presence of $AlCl_3$ and further subsequent reaction of the cyano-group results in the formation of an imino ether upon MeOH addition.

Introduction

2,3-Dichloro-5,6-dicyano-1,4-quinone (DDQ) has been widely used as a convenient oxidant in the synthesis of polyaryl-compounds and these oxidative processes have been intensively studied.[1–10] Initial radical formation, to generate resonance stabilized intermediates, has been considered as the principle oxidation mechanism when employing DDQ.[11,12] On the other hand, 1,4-benzoquinones bearing electron-withdrawing groups are strong dienophiles and a few examples are known where DDQ adducts have been reported as precursors formed during the aromatization of saturated compounds.[13–15]

Recently, the formation of unique DDQ-linked products, a C_2 symmetric hexapyrrole[16] and bis-dipyrrin linked DDQ adducts (bDLDAs) were reported (Fig. 1).[17] These DDQ-linked products were isolated during DDQ-oxidations of the corresponding tripyrromethane and dipyrromethanes under aerobic conditions. When the dipyrromethane contained an electron-withdrawing group such as pentafluorophenyl or 2,6-dichlorophenyl at the *meso*-position, the DDQ adducts were obtained in reasonable yields. Furthermore, refluxing these bDLDAs, in the presence of a Lewis acid and nucleophiles, produced atypical dipyrrin compounds as shown in Scheme 1. Compounds **1a** and **1b** formed, in higher yields than **1c**, were further employed in the synthesis of unusual dipyrrin compounds when reacted with nucleophiles. Thus **2a-1** and **2b-1** were formed when a THF solution of DDQ adducts **1a** and **1b** was refluxed in the presence of $AlCl_3$ and methanol. The mechanism can be rationalized as a ring opening and reclosing process, as shown in Scheme 2. Similarly, **2a-2** was prepared by treatment of **1a** with butyl alcohol. The compounds are unique and their synthetic procedures are rather facile. In this article, we report crystal structures of

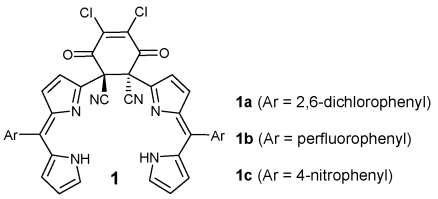
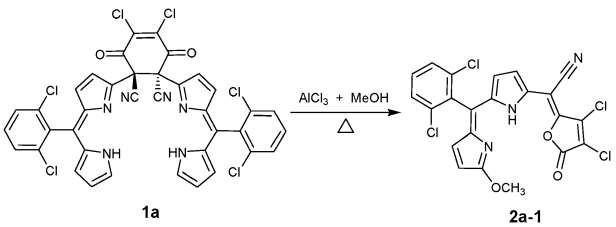
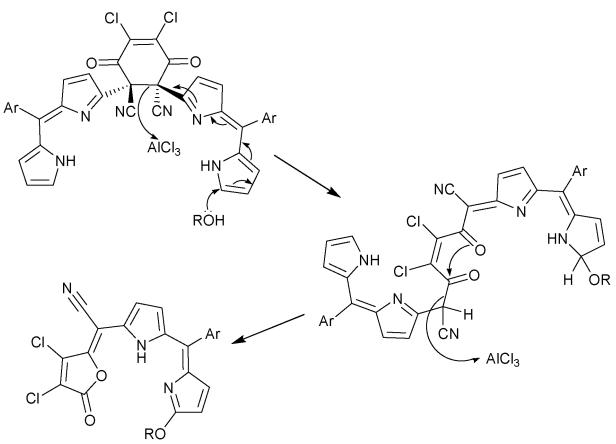


Fig. 1 bDLDAs (**1a–1c**).



Scheme 1 Formation of **2a-1** from **1a**.



Scheme 2 A possible mechanism for the formation of **2** from **1**.

[a] *Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T1Z1, Canada. E-mail: david.dolphin@ubc.ca; Fax: +1 6048229678; Tel: +1 6048224571*
[b] *Division of Advanced Materials Science, Pohang University of Science and Technology, San 31 Hyojadong, Pohang 790-784, Republic of Korea. E-mail: jyshin@postech.ac.kr; Fax: +82 542798138; Tel: +82 542798129*

† Electronic supplementary information (ESI) available: NMR spectra and crystallographic data. CCDC 750127 and 750128. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1nj20415g

the compounds **2a-2** and **2b-1** and formation of a furanone dipyrrin imino ether **3** as an additional product. Further treatment of **2a-1** with HCl and MeOH in the presence of silica gel resulted in the formation of the imino ether **3**.

Experimental section

General consideration

All reagents were either prepared following literature methods or purchased from commercially available suppliers and used without further purification. Column chromatography was performed on silica gel.

Physical measurements

All NMR spectra of the compounds were measured in CD_2Cl_2. ^{1}HNMR, ^{13}CNMR, ^{19}FNMR and 2D-NMR spectra were recorded using Bruker 300 and 400 spectrometers (CD_2Cl_2: 5.32 and 54.00 ppm for ^{1}H and ^{13}C, respectively). Mass spectra were determined on a time-of-flight (TOF) spectrometer equipped with an ESI ion source.

X-Ray crystallography

The X-ray data were collected on a Bruker X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation. All data collections were performed at 173 ± 0.1 K. Corrections were applied for Lorentz and polarization effects. All structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically and All C–H hydrogen atoms were placed in calculated positions but were not refined. The N–H hydrogen atoms were located in a difference map and refined isotropically.

General synthetic procedure of compounds 1a–1c

2,6-Dichlorophenyl, perfluorophenyl, and 4-nitrophenyl dipyrromethane were prepared by following the original method.[18] DDQ (2.29 g, 10.09 mmol) was added to a CH_2Cl_2 (150 mL) solution of dichlorophenyl dipyrromethane (1.12 g, 3.85 mmol). After stirring for 2 days, the reaction mixture was concentrated and column chromatographed on silica gel using neat CH_2Cl_2 as an eluent. The desired product **1a** followed by typical oxidized dipyrromethene was isolated first as a red and second a yellow fraction, in *ca.* 8% (124 mg) and 30% (330 mg) yields, respectively. Compounds **1b** and **1c** were prepared by the same method in 25% and 5% yields.

4,5-Dichloro-1,2-bis-{5-[(2,6-dichlorophenyl)-(1*H*-pyrrol-2-yl)-methylene]-5*H*-pyrrol-2-yl}-3,6-dioxo-cyclohex-4-ene-1,2-dicarbonitrile 1a. (124 mg, 8%) red solid; δ_H (400 MHz, CD_2Cl_2) 11.18 (bs, 2H, NH), 7.64 (m, 2H, α-CH), 7.55–7.40 (m, 6H, J = 8.0 Hz, Ph-H), 6.79 (d, 2H, J = 4.3 Hz, β-CH), 6.73 (d, 2H, J = 4.3 Hz, β-CH), 6.42 (m, 4H, β-CH); δ_C (100 MHz, CD_2Cl_2) 176.7, 156.0, 146.8, 142.8, 141.8, 136.7, 136.0, 135.7, 134.9, 134.2, 131.6, 131.5, 128.8, 128.7, 126.2, 122.0, 114.6, 114.3, 30.3; m/z HRESIMS, calcd. for $C_{38}H_{19}N_6O_2{}^{35}Cl_5{}^{35}Cl$ ($[M + H]^+$): 802.9691; found 802.9671.

4,5-Dichloro-3,6-dioxo-1,2-bis-{5-[pentafluorophenyl-(1*H*-pyrrol-2-yl)methylene]-5*H*-pyrrol-2-yl}-cyclohex-4-ene-1,2-dicarbonitrile 1b. (407 mg, 25%) Red solid; δ_H (400 MHz, CD_2Cl_2) 11.23 (bs, 1H, NH), 7.69 (s, 2H, α-CH), 6.86 (s, 4H, β-CH), 6.57 (m, 2H, β-CH), 6.47 (m, 2H, β-CH); δ_F (282.4 MHz, CD_2Cl_2) −138.53 (d, 2F, J = 23 Hz, *o*-F), −139.25 (d, 2F, J = 23 Hz, *o*-F), −152.03 (t, 2F, J = 21 Hz, *p*-F), −161.18 (m, 2F, *m*-F), −161.48 (m, 2F, *m*-F); δ_c (100 MHz, CD_2Cl_2) 176.7, 157.2, 147.2, 146.6, 144.0, 143.1, 141.3, 139.5, 136.9, 136.1, 131.5, 130.6, 126.9, 122.7, 115.2, 114.0, 61.5; m/z HRESIMS, calcd. for $C_{38}H_{13}N_6O_2F_{10}{}^{35}Cl_2$ ($[M + H]^+$): 845.0317; found 845.0303.

4,5-Dichloro-1,2-bis-{5-[(4-nitrophenyl)-(1*H*-pyrrol-2-yl)-methylene]-5*H*-pyrrol-2-yl}-3,6-dioxo-cyclohex-4-ene-1,2-dicarbonitrile 1c. (73 mg, 5%) Red solid; δ_H (400 MHz, CD_2Cl_2) 11.40 (bs, 2H, NH), 8.34 (d, 4H, J = 7.8 Hz, Ph-H), 7.72 (t, 4H, J = 7.8 Hz, Ph-H), 7.67–7.77 (m, 4H, α-CH), 6.83 (dd, 4H, J = 8.0, 3.4 Hz, β-CH), 6.54 (d, 2H, J = 3.4 Hz, β-CH), 6.47 (m, 2H, β-CH); δ_c (100 MHz, CD_2Cl_2) 176.7, 155.5, 149.4, 146.6, 145.6, 143.0, 142.9, 137.9, 135.5, 132.4, 132.3, 128.2, 123.6, 121.6, 114.9, 114.4, 33.9.

General synthetic procedure of compounds 2a-1, 2b-1, and 2b-2

$AlCl_3$ (600 mg) in MeOH (30 mL) was added to a THF (70 mL) solution of **2a-1** (108 mg, 134.6 μmol). After refluxing for 2 days, the reaction mixture was poured into water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4, filtered, and evaporated to dryness. The residue was column chromatographed on silica gel using CH_2Cl_2. The fastest pink fraction was collected and recrystallized from CH_2Cl_2 and hexane (20 mg, 30%). Similarly, compounds **2b-1** and **2a-2** were prepared by reactions with MeOH and butyl alcohol in 36% and 22% yields, respectively.

(3,4-Dichloro-5-oxo-5*H*-furan-2-ylidene)-{5-[(2,6-dichloro-phenyl)-(5-methoxy-1*H*-pyrrol-2-yl)-methylene]-5*H*-pyrrol-2-yl}-acetonitrile 2a-1. (20 mg, 30%) Purple solid; δ_H (400 MHz, CD_2Cl_2) 12.43 (bs, 1H, NH), 7.49 (d, 2H, J = 8.0 Hz, Ph-H), 7.40 (t, 1H, J = 8.0 Hz, Ph-H), 6.99 (m, 1H, J = 4.0 Hz, β-CH), 6.57 (d, 2H, J = 4.0 Hz, β-CH), 6.32 (d, 2H, J = 4.0 Hz, β-CH), 6.05 (d, 2H, J = 4.0 Hz, β-CH), 4.29 (s, 3H, Me); δ_C (100 MHz, CD_2Cl_2) 178.4, 160.2, 149.8, 145.0, 140.6, 138.8, 137.1, 136.9, 134.2, 131.24, 129.5, 128.8, 124.2, 122.7, 120.7, 118.0, 114.0, 91.9, 58.4; m/z HRESIMS, calcd. for $C_{22}H_{12}N_3O_3{}^{35}Cl_4$ ($[M + H]^+$): 505.9633; found 505.9636.

(3,4-Dichloro-5-oxo-5*H*-furan-2-ylidene)-{5-[(5-methoxy-1*H*-pyrrol-2-yl)-pentafluorophenyl-methylene]-5*H*-pyrrol-2-yl}-acetonitrile 2b-1. (26 mg, 36%) Purple solid; δ_H (400 MHz, CD_2Cl_2) 12.46 (bs, 1H, NH), 7.02 (m, 1H, J = 3.0 Hz, β-CH), 6.67 (d, 1H, J = 4.9 Hz, β-CH), 6.39 (d, 1H, J = 4.8 Hz, β-CH), 6.17 (d, 1H, J = 3.9 Hz, β-CH), 4.29 (s, 3H, Me); δ_F (282.4 MHz, CD_2Cl_2) −139.69 (dd, 2F, J = 32, 21 Hz, *o*-F), −153.30 (t, 1F, J = 21 Hz, *p*-F), −161.90 (m, 2F, *m*-F); δ_C (100 MHz, CD_2Cl_2) 136.9, 129.7, 123.6, 120.5, 118.2, 113.9, 113.2, 58.6 (Phenyl-H peaks are broaden due to the C–F couplings).

{5-[(5-Butoxy-1*H*-pyrrol-2-yl)-(2,6-dichloro-phenyl)-methylene]-5*H*-pyrrol-2-yl}-(3,4-dichloro-5-oxo-5*H*-furan-2-ylidene)-acetonitrile 2a-2. (16 mg, 22%) Purple solid; δ_H (400 MHz, CD_2Cl_2) 12.5 (bs, 1H, NH), 7.48 (d, 2H, J = 8.6 Hz, Ph-H), 7.39 (t, 1H, J = 7.9 Hz, Ph-H), 6.99 (m, 1H, β-CH), 6.55 (d, 1H,

J = 5.0 Hz, β-CH), 6.32 (d, 1H, J = 4.7 Hz, β-CH), 6.03 (m, 1H, β-CH), 4.68 (t, 2H, J = 5.9 Hz, $OCH_2CH_2CH_2CH_3$), 1.85 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.54 (m, 2H, $OCH_2CH_2CH_2CH_3$), 1.00 (t, 3H, J = 7.4 Hz, $OCH_2CH_2CH_2CH_3$); δ_C (100 MHz, CD_2Cl_2) 178.0, 160.1, 150.2, 145.1, 140.6, 138.7, 136.9, 134.3, 131.2, 129.3, 128.8, 123.7, 123.1, 122.3, 120.6, 118.0, 114.0, 91.9, 71.1, 31.4, 20.0, 14.2.

Synthesis of 2-(3,4-dichloro-5-oxo-5*H*-furan-2-ylidene)-2-{5-[(2,6-dichloro-phenyl)-(5-methoxy-1*H*-pyrrol-2-yl)-methylene]-5*H*-pyrrol-2-yl}-acetimidic acid methyl ester (3)

HCl was added to a MeOH and CH_2Cl_2 (1 : 1) solution of compound **2-1** (20 mg, 19.8 μmol) until the pH value of the solution reached 5. The resulting solution was stirred for 2 days and evaporated to remove the solvent. Compound **3** was separated by column chromatography on silica gel using 10% MeOH in CH_2Cl_2 as an eluent. (9.8 mg, 46%), yellowish red solid; δ_H (400 MHz, CD_2Cl_2) 12.15 (bs, 1H, NH), 7.90 (bs, 1H, NH), 7.52 (d, 2H, J = 8.8 Hz, Ph-H), 7.45 (t, 1H, J = 7.8 Hz, Ph-H), 7.02 (d, 1H, J = 4.4 Hz, β-CH), 6.63 (d, 1H, J = 4.9 Hz, β-CH), 6.52 (d, 1H, J = 5.4 Hz, β-CH), 5.91 (d, 1H, J = 4.4 Hz, β-CH), 3.94 (s, 3H, Me), 3.82 (s, 3H, Me); m/z HRESI (+)MS, calcd. for $[C_{23}H_{14}N_3O_4{}^{35}Cl_4]^+$: 535.9895; found 537.9883.

Results and discussion

Compounds **1a–1c** were prepared by treating saturated CH_2Cl_2 solutions of pentafluorophenyl, 2,6-dichlorophenyl, and 4-nitrophenyl substituted dipyrromethanes with 2 equivalents of DDQ. The solubility of compound **1a** in typical organic solvents is lower than **1b** and much of the former was lost during column chromatography on silica gel (the yield was 8% *versus* 25% for **1b**). **1c** was also obtained in a yield of 5%.[19] ^{1}H NMR spectra of bDLDAs (**1a–1c**) are shown in Fig. 2. The amino-Hs on the pyrrole rings of all the DDQ adducts are highly downfield-shifted as a result of the intramolecular hydrogen-bonding (11.18, 11.23, and 11.40 ppm for **1a**, **1b**, and **1c**, respectively).

1a and **1b** were each separately refluxed overnight in THF with methanol, *n*-butyl alcohol, *n*-octyl alcohol, or *n*-hexyl thiol in the presence of $AlCl_3$. During these reactions the red-colored solutions gradually changed to purple as the reaction progressed. TLC monitoring of the reactions showed several unstable by-products most of which were found to have decomposed after washing with water and extraction with CH_2Cl_2. When bulky aryl alcohols, such as 2,3,4,5-tetrachlorophenol and 2,3-difluorophenol, were employed, much of the starting material (DDQ-adduct) was converted to the α-free dipyrromethene and eluted as the first red fraction during column chromatography on silica gel. The desired bright purple fractions were separated using a gradient elution with increasing amounts of MeOH in CH_2Cl_2. On the other hand, alkyl chain alcohol adducts were obtained in higher yields without the formation of decomposed dipyrrins. In these cases, the furanyl compounds were easily separated using neat CH_2Cl_2 during column chromatography owing to their relatively low polarity.

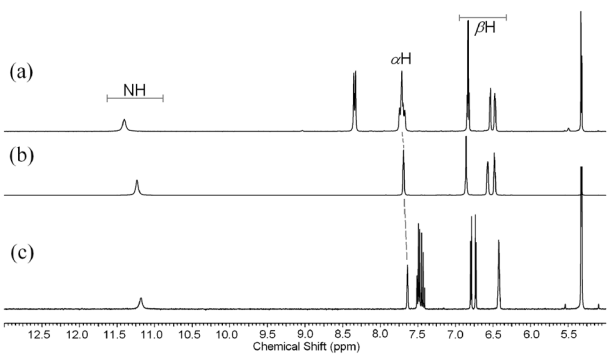


Fig. 2 ^{1}H NMR spectra of **bDLDAs** in CD_2Cl_2; DDQ adducted (a) 4-nitrophenyl, (b) pentafluorophenyl, and (c) 2,6-dichlorophenyl dipyrrins.

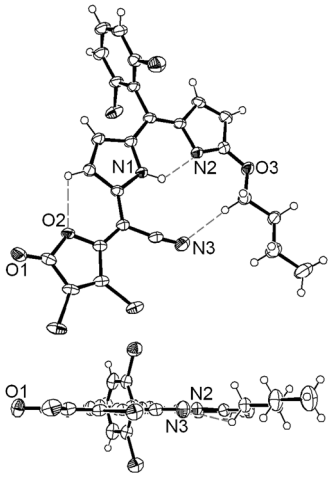


Fig. 3 ORTEP views of **2a-2** with thermal ellipsoids shown at 50% probability. Intramolecular hydrogen bonds are denoted with dashed lines.

A possible mechanism is shown in Scheme 2. Nucleophilic attack by the alcohol followed by rearrangement leads to ring opening (at the sp^3C–sp^3C bond of the DDQ moiety) in the presence of a Lewis acid. Nucleophilic ring-closing of the keto-O and bond cleavage between the keto-C and sp^3C result in the formation of the final keto-furanyl dipyrrin **2**.

Fortunately, single crystals of **2a-2** (Fig. 3) and **2b-1** (Fig. 4) were successfully grown by vapor addition of hexane into a CH_2Cl_2 solution.‡ The crystal structure of **2b-1** (Fig. 4), having a methoxy group, shows a similar structure to that of **2a-1** which we reported earlier.[17] On the other hand, the crystal structure of **2a-2** exhibits a different configuration from that of compounds **2a-1** and **2b-1** (Fig. 5). While the O atom in the ring is oriented towards the nitrogens of the dipyrrin

‡ Crystal data of **2a-2**: $C_{25}H_{17}Cl_4N_3O_3$, T = 173 K, M = 549.22, triclinic, $P\bar{1}$ (no. 2), a = 7.5524(4) Å, b = 12.9084(7) Å, c = 13.1120(7) Å, α = 102.326(2)°, β = 94.333(2)°, γ = 98.378(2)°, V = 1227.94(11) Å^3, D_c = 1.485 gcm^{-3}, Z = 2, R_1 = 0.0409 [$I > 2.00\sigma(I)$], wR_2 = 0.1179 (all data), GOF = 1.075, CCDC 750127.

Crystal data of **2b-1**: $C_{22}H_8Cl_2F_5N_3O_3$, T = 173 K, M = 528.21, triclinic, $P\bar{1}$ (no. 2), a = 7.0689(13) Å, b = 9.6348(19) Å, c = 16.074(3) Å,α = 94.959(7)°, β = 95.467(7)°, γ = 106.429(7)°, V = 1037.9(3) Å^3, D_c = 1.690 g cm^{-3}, Z = 2, R_1 = 0.0347 [$I > 2.00\sigma(I)$], wR_2 = 0.1019 (all data), GOF = 0.990, CCDC 750128.

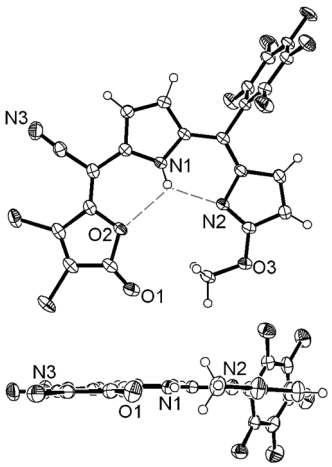


Fig. 4 ORTEP views of **2b-1** with thermal ellipsoids shown at 50% probability. Intramolecular hydrogen bonds are denoted with dashed lines.

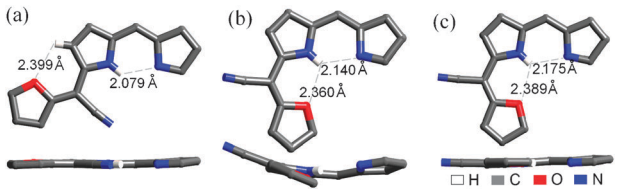
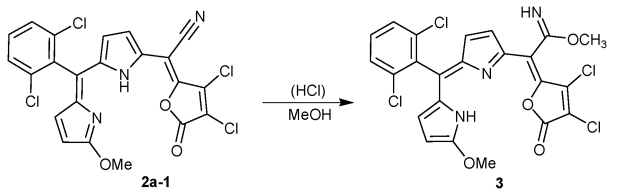


Fig. 5 Comparison of the different orientations of (a) **2a-2**, (b) **2a-1** and (c) **2b-1**.

moiety in the latter, the former has the cyclic ring inverted and facing in the opposite direction. This results first from the inclusion of a longer alkyl chain which produces an intramolecular CH–N hydrogen-bond between the *meso*-cyano-N atom and the butoxy-$^1CH_2$ group. This H-bond formation renders the original N–H···O hydrogen-bond weaker, allowing rotation of the furanyl ring to generate a new hydrogen-bond (C–H···O) between the furanyl-O and β-CH on the neighboring pyrrole ring (Fig. 3). Disruption of the initial N–H···O hydrogen-bond causes the NH peak to be sharper in its ^{1}H NMR spectrum (Fig. 6). Similarly, the $^1CH_2$-peaks of the alkyl chain are shifted down-field (4.68 ppm).

2a-1 was converted to compound **3** by MeOH addition in the presence of a minute amount of HCl. As in a Pinner reaction,[20] the cyano group was converted to an imino ether *via* imino ether hydrolysis. The high resolution mass spectrum of **3** confirms the structure described in Scheme 3 ($C_{23}H_{14}N_3O_4{}^{35}Cl_4$; calculated and found masses are (*m*/*z*) 535.9895 and 537.9883, respectively). In addition, a CD_2Cl_2



Scheme 3 Formation of **3** from **2a-1**.

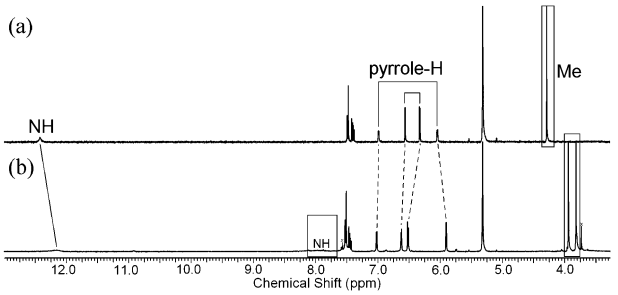


Fig. 7 Comparison of the ^{1}H NMR spectra of **2a-1**(a) and **3**(b).

solution of **3** afforded a broad singlet and a sharp singlet for the peaks of the newly formed NH and methoxy groups, in the ^{1}H NMR spectrum (Fig. 7). The original methoxy-group and the other β-Hs become shielded as a result of the stronger electron-withdrawing group, resulting in their upfield-shifts while the neighboring β-Hs' peaks are shifted downfield.

Conclusions

In summary, variously substituted furanone dipyrrins have been prepared using a facile synthetic method. Their imino ethers were obtained by further treatment of compound **2a-1** with an acid and MeOH in the presence of HCl. These compounds are expected to be useful as building blocks in developing fully-conjugated pathways and enhancing planarity throughout the main skeleton of interesting heterocyclic compounds.

Acknowledgements

Financial support for this work was provided by the Natural Sciences and Engineering Research Council (NSERC) of Canada. We thank Dr Brian O. Patrick from the X-ray crystallography laboratory of the Department of Chemistry at UBC.

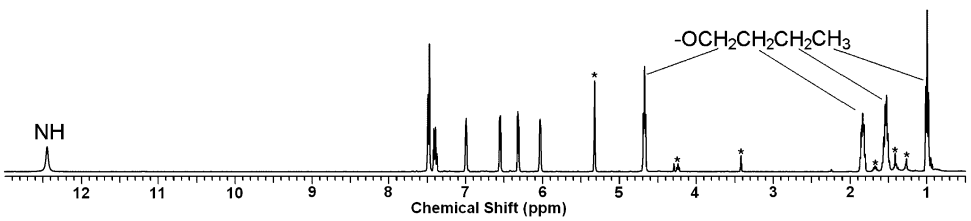


Fig. 6 ^{1}H NMR spectrum of **2a-2** in CD_2Cl_3; solvent impurities are identified by *.

Notes and references

1 D. Walker and J. D. Hiebert, *Chem. Rev*., 1967, **67**, 153–195.
2 J. S. Lindsey, I. C. Schreiman, H. C. Hsu, P. C. Kearney and A. M. Margueretaz, *J. Org. Chem*., 1987, **52**, 827–836.
3 L. Yu, K. Muthukumaran, I. V. Sazanovich, C. Kirmaier, E. Hindin, J. R. Diers, P. D. Boyle, D. F. Bocian, D. Holten and J. S. Lindsey, *Inorg. Chem*., 2003, **42**, 6629–6647.
4 G. R. Geier III, J. F. B. Chick, J. B. Callinan, C. G. Reid and W. P. Auguscinski, *J. Org. Chem*., 2004, **69**, 4159–4169.
5 L. Capella, P. C. Montevecchi and D. Nanni, *J. Org. Chem*., 1994, **59**, 7379–7382.
6 C. Brücker, V. Karunaratne, S. J. Rettig and D. Dolphin, *Can. J. Chem*., 1996, **74**, 2182–2193.
7 J. S. Lindsey, *The Porphyrin Handbook*, ed. K. M. Kadish, K. M. Smith and R. Guilardm, Academic Press, San Diego, CA, 2000.
8 Z. Gross, N. Galili and I. Saltsman, *Angew. Chem., Int. Ed*., 1999, **38**, 1427–1429.
9 J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc*., 2001, **123**, 7190–7191.
10 T. E. Wood and A. Thompson, *Chem. Rev*., 2007, **107**, 1831–1861.
11 G. G. Mohamed, F. A. Nour El-Dien and E. U. Farag, *Spectrochim. Acta, Part A*, 2006, **65**, 11–19, and its references.
12 J. H. P. Utley and G. G. Rozenberg, *J. Appl. Electrochem*., 2003, **33**, 525–532.
13 X. Zhou, M. Kitamura, B. Shen, K. Nakajima and T. Takahashi, *Chem. Lett*., 2004, **33**, 410–411.
14 M. T. Stone and H. L. Anderson, *J. Org. Chem*., 2007, **72**, 9776–9778.
15 T. Takahashi, K. Kashima, S. Li, K. Nakajima and K.-I. Kanno, *J. Am. Chem. Soc*., 2007, **129**, 15752–15753.
16 J.-Y. Shin, S. S. Hepperle, B. O. Patrick and D. Dolphin, *Chem. Commun*., 2009, 2323–2325.
17 J.-Y. Shin, B. O. Patrick and D. Dolphin, *Org. Biomol. Chem*., 2009, **7**, 2032–2035.
18 C. H. Lee and J. S. Lindsey, *Tetrahedron*, 1994, **50**, 11427–11440.
19 The observed yields, *o*-F > *o*-Cl > *p*-NO_2 can be rationalized as a result of the effectiveness of the electronic and steric configurations of the EWGs; J.-Y. Shin, H. Furuta, K. Yoza, S. Igarashi and A. Osuka, *J. Am. Chem. Soc*., 2001, **123**, 7190–7191; R. Taniguchi, S. Shimizu, M. Suzuki, J.-Y. Shin, H. Furuat and A. Osuka, *Tetrahedron Lett*., 2003, **44**, 2505–2507; J.-Y. Shin, S. S. Hepperle and D. Dolphin, *Tetrahedron Lett*., 2009, **50**, 6909–6912.
20 L. Kürti and B. Czakó, *Strategic Applications of Named Reactions in Organic Synthesis*, Elsevier Academic Press, San Diego, CA, 2005.