Reaction of N^1,N^2-diarylamidines with dicyanomethylene compounds

Dietrich Döpp,*[a] Mohsen A. Gomaa,[a,b] Gerald Henkel[a] and Ahmed M. Nour El-Din[b]

[a] *Divisions of Organic and Solid State Chemistry, Gerhard-Mercator-University – GH Duisburg, D-47048 Duisburg, Germany*
[b] *Chemistry Department, Faculty of Science, El-Minia University, El-Minia, Arab Republic of Egypt*

2-Arylamino-2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)ethanenitriles 6a–c together with the corresponding formanilides 7a–c have been obtained from the reaction of N^1,N^2-diarylformamidines 1a–c with 2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile 2 in ethyl acetate solution, while the analogous N^1,N^2-diarylacetamidines 8b–e with 2 gave indeno[1,2-*d*]azepines 17b–e and in two cases 2-arylamino-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)ethanenitriles 6b,c as minor products. In contrast, 2-oxospiro[(2,3-dihydro-1*H*-indole)-3,4′-(1′,2′,3′,4′-tetrahydropyridine)]-5′-carbonitriles 22b,c were obtained from the reaction of 8b,c with 2-(2-oxo-2,3-dihydro-1*H*-indol-2-ylidene)propanedinitrile 18. The structure assignment of spiro compound 22b has been confirmed on the basis of an X-ray crystal structure determination.

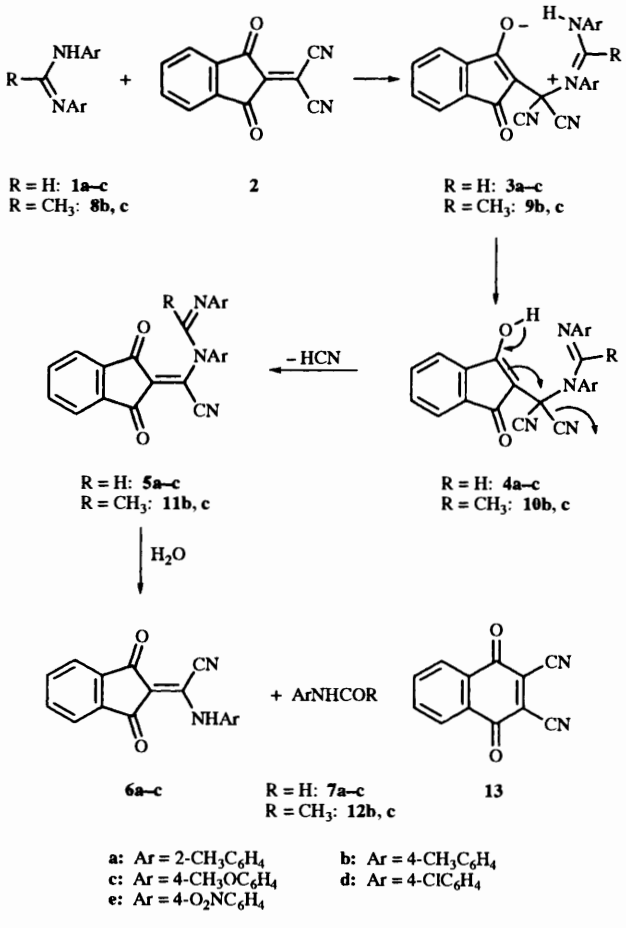
Introduction

Junek and co-workers have reported that 2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidine)propanedinitrile **2**, previously referred to as 2-(dicyanomethylene)indanedione, reacts with diethylamine,[1] primary aromatic amines,[2] 2-aminonaphtho-1,4-quinone,[3] 1-aminoanthraquinone[3] and hydrazines[2] by a Michael-addition–elimination-type sequence with loss of one cyano group to give the corresponding 2-arylamino-(1,3-dioxo-2-indanylidene)ethanenitriles. 1,2-Phenylenediamines similarly effect the replacement of both cyano groups to give 2-(1,3-dioxoindan-2-ylidene)benzimidazolines together with (11*H*-indeno[1,2-*b*]quinoxalin-11-ylidene)propanedinitriles.[4] The origin of the latter compounds has not been unravelled by the authors,[4] however, simple MO calculations have shown that the Michael-addition–elimination sequence was preferred over attack at the carbonyl group leading to the formation of imines.[5] On the other hand, secondary and tertiary arylamines react (*via* a *p*-carbon atom) with **2** *via* replacement of one cyano group by a phenyl ring.[6] Recently Grigg and Mongkolaussavaratana[7] reported that α-amino acids and their esters also react with **2** by a Michael-addition–elimination sequence with replacement of one cyano group by the amino function.

Results and discussion

In the light of the aforementioned findings, we undertook to investigate the reactions of open chain amidines with **2**. N^1,N^2-Diarylformamidines **1a–c** reacted rapidly with **2** in ethyl acetate under reflux (for **1a**), or at room temperature (for **1b**, **1c**), to give 2-arylamino-2-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)ethanenitriles **6a** (19%), **6b** (30%) and **6c** (47%), respectively, together with the corresponding formanilides **7a** (44%), **7b** (80%) and **7c** (75%) (Scheme 1). Products **6a–c**[2,8] and the formanilides[9–11] were identified by comparison of their melting points with those reported for authentic samples.

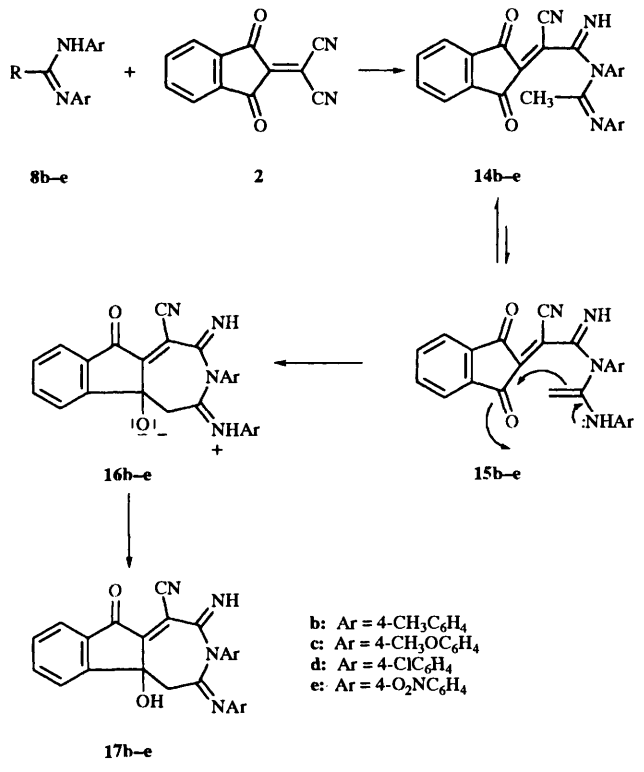
These results indicate that formamidines **1a–c** with **2** ultimately form the same products as the corresponding primary amines, that is by a Michael-addition–elimination-type sequence similar to that one well documented[1–7] through a nucleophilic attack of N^2 on the *exo*-methylene carbon atom of



Scheme 1

2 to form intermediates **3a–c** and **4a–c**, which *via* elimination of HCN give **5a–c**. The latter in turn, upon chromatographic work-up, undergo hydrolysis to form **6a–c** and **7a–c**.

On the other hand, N^1,N^2-diarylacetamidines **8b–e** reacted with **2** in ethyl acetate at room temperature (**8b–d**) or at reflux (**8e**) for 24 h by formation of the novel indeno[1,2-*d*]azepines



Scheme 2

17b–e (in 20–61% yield) (Scheme 2). In two cases (**b**,**c**), the ethanenitriles **6b**,**c** were also formed in minor amounts.

The IR spectra of **17b–e** showed strong absorptions between 3310 and 3315 cm^{-1} for OH and between 3240 and 3225 cm^{-1} for NH with further bands in the range 2190–2195 cm^{-1} for CN and 1715–1720 cm^{-1} for CO. ^1H NMR AB patterns with δ_A in the range 3.14–3.35 and δ_B between 2.63 and 2.79 with $|^2J|$-values between 17.20 and 17.85 Hz are assigned to the C-5 methylene group adjacent to the chiral carbon atom C-5a. The presence of this methylene group is also evident from the ^{13}C-DEPT-spectra exhibiting negative signals between δ 32.80 and 32.50. The broad-band ^1H-decoupled ^{13}C-NMR spectra showed one signal each between δ 59.50 and 61.20 for C-5a bearing the hydroxy group and one signal each between δ 115.0 and 117.40 for the cyano group.

The most plausible origin of the methylene group certainly is the acetyl-derived methyl group in the acetamidines **8b–e**, and the formation of the indeno[1,2-*d*]azepines **17b–e** can be rationalized as follows: initial nucleophilic attack by N^2 of **8b–e** on one nitrile carbon of **2** gives rise to **14b–e** which must be envisaged as being in equilibrium with the tautomers **15b–e**. These tautomers, being essentially ketene aminals, exhibit nucleophilic character at the terminal methylene carbon atom attacking C-1 of **2** and thereby **17b–e** are formed. A minor fraction of **8b**,**c** undergoes the Michael-addition–elimination sequence giving **6b**,**c** together with **12b**,**c** after hydrolysis.

Since **8b–e** are to be considered also as electron donors, the *a priori* possibility existed that **2** underwent an electron transfer mediated rearrangement into naphtho-1,4-quinone-2,3-dicarbonitrile **13**.[12,13] Consequently, **8b** as a sample was allowed to react with **13** under the same conditions as employed for the reactions of **2** with **8b–e**. All that was obtained, however, was a green precipitate, which was assigned to be a solid charge transfer complex of **13** and **8b** and no indenoazepine had been formed definitely. This result provides support for structures **17b–e** originating from **8b–e** and **2** without prior isomerization of the latter.

From earlier work by Sterk and Junek[5] attack of the methylene carbon of **15** on indenyl-C-2, the position β to the remaining nitrile, should be expected rather than attack at one

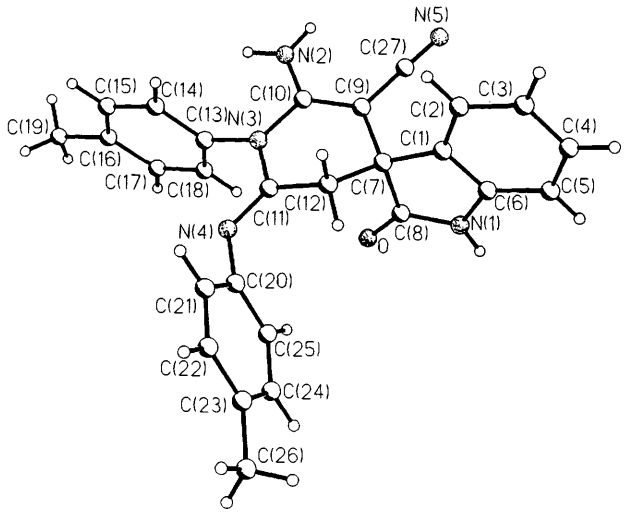


Fig. 1 Molecular structure of **22b** in the crystal (the crystallographic numbering does not reflect the systematic numbering)

of the oxo groups, resulting in a spiro structure related to **22**, to be discussed below. However, the shift difference observed in the methylene signals and the number of signals attributable to aryl-carbon atoms linked to hydrogen excluded a (necessarily more symmetric) spiro structure for compounds **17**.

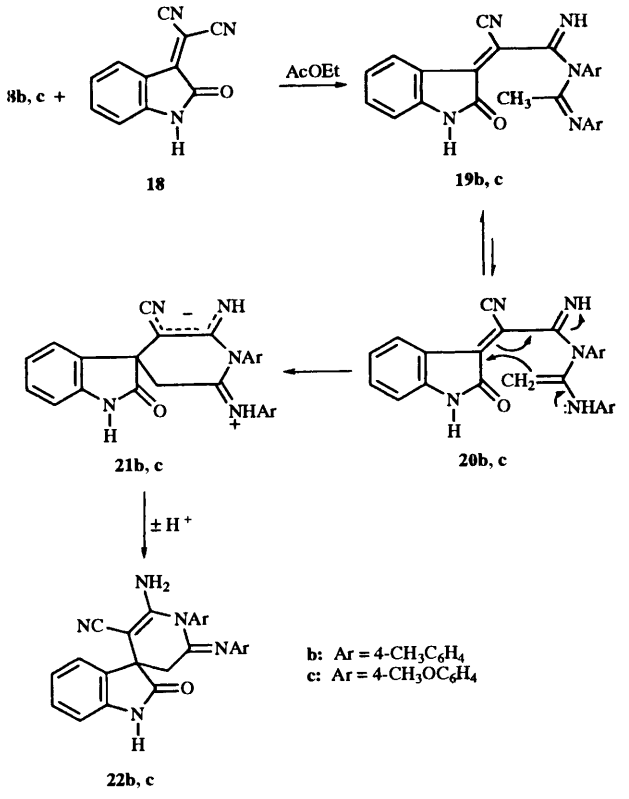
For comparison, it seemed appropriate to investigate the reaction, if any, of **8** with the propanedinitrile **18**. To this end, equimolar amounts of **18** and **8b**,**c** were kept in ethyl acetate solution at reflux and afforded solid products in 53 and 61% yield, respectively, which were demonstrated to have structures **22b** and **22c**, respectively.

The IR spectra (KBr) showed typical absorptions between 3460 and 3310 cm^{-1} (NH_2), 3200 cm^{-1} (NH), 2190 (CN) and 1720 cm^{-1} (C=O). ^1H NMR AB patterns with δ_A = 2.35 and δ_B = 2.16 and $|^2J|$ = 15.28 Hz again indicated the presence of a CH_2 group next to a chiral carbon atom in addition to signals at δ 4.62 and 8.67 for NH_2 and NH protons, respectively. The ^{13}C NMR DEPT spectrum showed a negative signal at δ = 32.62 confirming the presence of a CH_2 group and a ^{13}C signal at δ 45.90 was assigned to the spiro carbon atom. An unambiguous structure assignment was made through the X-ray crystal structure analysis of **22b** (Fig. 1). Note that **22b** has been crystallized and analysed as a stoichiometric solvate with three molecules of chloroform.

To rationalize the formation of **22b**,**c**, it may be proposed that nucleophilic attack of N^2 of **8b**,**c** on CN of **18** forms **19b**,**c** being in equilibrium with **20b**,**c** (Scheme 3). The nucleophilic methylene carbon of the latter obviously prefers attacking at C-3 instead of C-2 of the indolinone moiety in **20** forming **21b**,**c** which is ultimately isolated as **22b**,**c**. Lack of attack at C-2 is plausibly due to the amide carbonyl nature and thus reduced electrophilic character of the latter compared with carbonyl reactivity in **15**.

Experimental

All the melting points were determined with a Reichert Thermovar hot stage microscope and are uncorrected. The IR spectra were recorded with a Perkin-Elmer 283 spectrophotometer using potassium bromide pellets. 300 MHz ^1H and 75 MHz $^{13}C(^1H)$ NMR spectra were recorded on a Bruker WM 300 instrument with TMS as internal reference, m = multiplet. *J* Values are measured in Hz. Mass spectra were obtained on a MAT 311 A instrument by EI at 70 eV in connection with an AMD DP-10 data processing system. Combustion analyses were carried out with a Carlo Erba Mod. 1106 CHN analyser. For preparative layer chromatography (PLC) air dried 1.0 mm thick layers of slurry applied silica gel Merck PF_{254} on 48 cm



Scheme 3

wide and 20 cm high glass plates were employed using the solvents listed for development. Zones were detected by quenching of indicator fluorescence upon exposure to 254 nm light, excarved and eluted with either ethyl acetate or acetone.

Starting materials

2-(1,3-Dioxo-2,3-dihydro-1*H*-inden-2-ylidene)propanedinitrile **2**,[14] 2-(2-oxo-2,3-dihydro-1*H*-indol-2-ylidene)propanedinitrile **18**,[14] N^1,N^2-diarylformamidines[15] **1a–c** and N^1,N^2-diarylacetamidines[16] **8b,e** were prepared according to the literature procedures quoted.

Reaction of N^1,N^2-diarylformamidines 1a–c with 2 (general procedure)

A solution of **2** (208 mg, 1.0 mmol) in ethyl acetate (30 cm^3) was added dropwise to a solution of formamidine **1a**, **1b** or **1c**, respectively (1.0 mmol) in ethyl acetate (10 cm^3) at room temperature, whereby the solution assumed a yellowish-brown colour. The reaction mixture was either left standing for 1 h (**1a,b**) or refluxed for 48 h (**1c**), concentrated and subjected to PLC using toluene–ethyl acetate (10 : 1) as developing solvent to give two zones. The faster moving one contained **6a**, **6b** or **6c**, respectively, while the second zone contained the corresponding formanilide **7a**, **7b** or **7c**. The zones were extracted, crystallized and identified as follows.

2-Methylphenylamino-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)ethanenitrile 6a. 55 mg (19%), yellow crystals (from acetonitrile), mp 182–184 °C (lit.,[8] 182 °C).

4-Methylphenylamino-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)ethanenitrile 6b. 85 mg (30%), yellow crystals (from cyclohexane), mp 208–210 °C (lit.,[8] 205–207 °C).

4-Methoxyphenylamino-(1,3-dioxo-2,3-dihydro-1*H*-inden-2-ylidene)ethanenitrile 6c. 143 mg (47%), yellow crystals (from ethanol), mp 203–207 °C (lit.,[8] 203–204 °C).

2′-Methylformanilide 7a. 59 mg (74%), colourless crystals, mp 57–60 °C (from light petroleum, bp 40–60 °C) (lit.,[9] 57–59 °C).

4′-Methylformanilide 7b. 108 mg (80%), colourless crystals, mp 53 °C (from light petroleum, bp 40–60 °C) (lit.,[10] 52 °C).

4′-Methoxyformanilide 7c. 114 mg (75%), colourless crystals, mp 81 °C (from light petroleum, bp 40–60 °C) (lit.,[11] 84–85 °C).

Reaction of N^1,N^2-diarylacetamidines 8b–e with 2 (general procedure)

To a stirred solution of each of the amidines **8b–e** in ethyl acetate (5 cm^3) a solution of **2** (208 mg, 1.0 mmol) in ethyl acetate (30 cm^3) was added dropwise at room temperature. After 10 min yellow crystals of **17b–d** precipitated (in the case of **17e** only after heating the mixture at reflux for 24 h) which were filtered off and crystallized from ethyl acetate. The filtrates were concentrated and the residues were subjected to PLC using toluene–ethyl acetate (2 : 1) as developing solvent to give one or two main zones; the faster moving one contained small amounts of **6b** or **6c**, respectively, while the more slowly moving zones contained **17b**, **17c**, **17d** or **17e**, respectively. Additional minor zones were discarded. Compounds **6b** and **6c** were collected and identified as before.

5a-Hydroxy-2-imino-3-(4-methylphenyl)-4-(4-methylphenylimino)-10-oxo-2,3,4,5,5a,10-hexahydroindeno[1,2-*d*]azepine-1-carbonitrile 17b

This compound was obtained as a colourless powder (266 mg, 60%), mp 284–286 °C (from ethyl acetate) (Found: C, 75.1; H, 4.9; N, 12.5. $C_{28}H_{22}N_4O_2$ requires C, 75.32; H, 4.97; N, 12.55%); ν_{max}(KBr)/cm^{-1} 3315 (OH), 3240 (NH), 2195 (CN) and 1720 (CO); δ_H(300 MHz, [$^2H_6$]DMSO) 2.23 (3 H, s, CH_3), 2.38 (3 H, s, CH_3), 3.20 (1 H, d) and 2.67 (1 H, d, *J* 17.2, 1-CH_2), 6.70, 6.83, 7.04, 7.31, 7.37 and 7.65 (all m, 12 aryl-H), 7.72 (2 H, br, NH and OH); δ_C(75 MHz, [$^2H_6$]DMSO) 20.45 (two CH_3), 33.65 (C-5), 53.44 (C-2), 61.17 (C-5a), 107.52 (C-10a), 117.27 (*C*N), 120.91, 124.52, 124.91, 128.41, 129.38, 129.66, 131.61, 135.97 (aryl-CH), 131.33 (C-5a), 134.17 and 134.78 (aryl-*C*–Me), 137.28 (C-9a), 145.45 and 147.54 (aryl-C–N), 166.03 (C-4), 166.28 (C-2) and 198.4 (C-10); *m*/*z* 446 (M^+, 94%), 403 (100), 374 (14), 364 (11), 312 (12), 297 (8), 285 (31), 271 (13), 236 (24), 107 (11), 91 (17), 65 (10) and 44 (10).

5a-Hydroxy-2-imino-3-(4-methoxyphenyl)-4-(4-methoxyphenylimino)-10-oxo-2,3,4,5,5a,10-hexahydroindeno[1,2-*d*]azepine-1-carbonitrile 17c

This compound was obtained (94 mg, 20%) as a colourless powder, mp 260–262 °C (from ethyl acetate) (Found: C, 69.9; H, 4.8; N, 12.0. $C_{28}H_{22}N_4O_4$ requires C, 70.28; H 4.63; N, 11.71%); ν_{max}(KBr)/cm^{-1} 3310 (OH), 3225 (NH), 2190 (CN) and 1720 (CO); δ_H(300 MHz, [$^2H_6$]DMSO) 3.14 (1 H, d) and 2.63 (1 H, d, $|^2J|$ 17.20, CH_2), 3.68 (3 H, s, OCH_3), 3.80 (3 H, s, OCH_3), 6.72, 6.77, 7.03, 7.32 and 7.66 (12 H, all m, aryl-H) and 7.84 (2 H, br, NH and OH); δ_C(75 MHz, [$^2H_6$]DMSO) 32.16 (C-5), 51.93 (C-1), 53.65 and 53.93 (OCH_3), 59.54 (C-5a), 106.04 (C-10), 115.83 (*C*N), 112.64, 112.89, 120.48, 123.08, 123.40, 128.55, 130.08 and 134.49 (all aryl-*C*H), 127.70 (C-5b), 133.28 (C-9a), 141.76 and 143.98 (aryl-*C*N), 153.46 (C-4), 157.13 and 158.90 (aryl-*C*–OCH_3), 164.78 (C-2) and 196.99 (C-10); *m*/*z* 478 (M^+, 14%), 435 (24), 396 (24), 148 (24), 123 (60), 108 (85), 80 (24), 66 (15) and 143 (100).

5a-Hydroxy-2-imino-3-(4-chlorophenyl)-4-(4-chlorophenylimino)-10-oxo-2,3,4,5,5a-10-hexahydroindeno[1,2-*d*]azepine-1-carbonitrile 17d

Colourless powder (347 mg, 75%), mp 299–300 °C (from ethyl acetate) (Found: C, 64.0; H, 3.3; N, 11.5. $C_{26}H_{16}Cl_2N_4O_2$ requires C, 64.06; H, 3.31; N, 11.50%); ν_{max}(KBr)/cm^{-1} 3310 (OH), 3225 (NH), 2195 (CN) and 1715 (CO); δ_H(300 MHz, [$^2H_6$]DMSO) 3.25 (1 H, d) and 2.65 (1 H, d, $|^2J|$ 17.25, CH_2), 6.78, 7.25, 7.54, 7.61, 7.63, 7.68 and 7.88 (all m, 12 aryl-H), 7.76 (2 H, br, OH and NH); δ_C(75 MHz, [$^2H_6$]DMSO) 32.15 (C-5), 51.89 (C-1), 59.72 (C-5a), 105.76 (C-10) 115.56 (*C*N), 121.38, 122.90, 123.40, 127.15, 128.65, 130.15 and 134.51 (all aryl-C–H), 125.18 (C-5b), 130.81 (C-2), 133.37 and 134.11 (aryl-*C*–Cl), 143.48 and 147.30 (aryl-*C*–N), 159.03 (C-4), 164.60 (C-2) and 196.46 (C-10); *m*/*z* 487 (M^+, 21%), 486 (40), 443 (100), 305 (26), 271 (22), 152 (18), 127 (15), 111 (25), 75 (14) and 43 (28).

5a-Hydroxy-2-imino-3-(4-nitrophenyl)-4-(4-nitrophenylimino)-10-oxo-2,3,4,5,5a-10-hexahydroindeno[1,2-*d*]azepine-1-carbonitrile 17e

Yellow crystals (311 mg, 61%), mp 300 °C (from ethyl acetate) (Found: C, 61.4; H, 3.4; N, 16.25. $C_{26}H_{16}N_6O_6$ requires C, 61.42; H, 3.17; N, 16.53%); ν_{max}(KBr)/cm^{-1} 3310 (OH), 3225 (NH), 2195 (CN) and 1720 (CO); δ_H(300 MHz, [$^2H_6$]DMSO) 3.35 (1 H, d) and 2.79 (1 H, d, $|^2J|$ 17.87, CH_2), 7.03, 7.13, 7.70, 7.90, 815 and 8.43 (all m, 12 aryl-H) and 7.85 (2 H, br, OH and NH); δ_C(75 MHz, [$^2H_6$]DMSO) 32.53 (C-5), 51.88 (C-1), 59.96 (C-5a), 105.74 (C-10a), 115.39 (C≡N), 120.46, 123.03, 123.16, 123.28, 123.44, 127.26, 130.37 and 134.64 (all aryl-*C*–H), 133.54 (C-5b), 141.16 and 141.23 (aryl-*C*–NO_2), 143.07 and 144.69 (aryl-*C*–N), 154.85 (C-9a), 159.13 (C-4), 164.49 (C-2) and 196.05 (C-10); *m*/*z* 508 (M^+, 5%), 481 (6), 465 (4), 300 (13), 208 (12), 183 (11), 163 (91), 138 (17), 117 (35), 104 (21), 92 (11), 76 (35), 66 (17) and 44 (100).

Reaction of 8b,c with 18

Solutions of acetamidines **8b,c** (1.5 mmol each) in ethyl acetate (10 cm^3) were added to solutions of **18** (1.5 mmol) in ethyl acetate (25 cm^3). The mixtures were heated at reflux for 1 h, concentrated and subjected to PLC using toluene–ethyl acetate (2:1) as the developing solvent. The main zones in either case contained compound **22b** or **22c**, respectively. All other zones contained too small amounts of material for successful characterization and were therefore discarded.

6′-Amino-1-(4-methylphenyl)-2′-(4-methylphenylimino)-2-oxospiro[(2,3-dihydro-1*H*-indole)-3,4′-(1′,2′,3′,4′-tetrahydropyridine)]-5′-carbonitrile 22b

This compound (343 mg, 53%) was obtained as colourless crystals, mp 263–267 °C (from chloroform) and dried under reduced pressure (Found: C, 74.7; H, 5.4; N, 16.0. $C_{27}H_{23}N_5O$ requires C, 74.80, H, 5.38; N, 16.16%); ν_{max}(KBr)/cm^{-1} 3400 (NH_2), 3200 (NH), 2190 (CN) and 1720 (CO); δ_H(300 MHz, $CDCl_3$) 2.16 (3 H, s, CH_3), 2.35 (3 H, s, CH_3), 2.90 (1 H, d) and 2.75 (1 H, d, $|^2J|$ 15.29, CH_2), 4.62 (2 H, s, NH_2), 6.40, 6.79, 6.87, 7.06 and 7.30 (all m, aryl-CH) and 8.67 (1 H, s, NH); δ_C(75 MHz, $CDCl_3$) 20.63 (*C*H_3), 21.23 (*C*H_3), 33.58 (C-3′), 45.99 (C-3 = C-4′), 57.55 (C-5′), 110.49, 120.21, 123.69 and 129.41 (all aryl-*C*H), 119.50 (*C*≡N), 130.80 (C-3a), 132.40 and 133.76 (aromatic *C*–Me), 139.33 and 140.23 (aromatic C–N), 145.60 (C-7a), 152.44 (C-2′), 156.33 (C-6′) and 179.24 (C-2); *m*/*z* 433 (M^+, 50%), 404 (35), 327 (9), 315 (7), 299 (13), 286 (8), 273 (11), 238 (12), 195 (17), 183 (16), 169 (11), 140 (10), 132 (100), 107 (32), 91 (82), 65 (38) and 44 (42).

6′-Amino-1-(4-methoxyphenyl)-2′-(4-methoxyphenylimino)-2-oxospiro[(2,3-dihydro-1*H*-indole)-3,4′-(1′,2′,3′,4′-tetrahydropyridine)]-5′-carbonitrile 22c

This compound (426 mg, 61%) was obtained as a colourless powder, mp 227–230 °C (from ethyl acetate–cyclohexane) (Found: C, 69.35; H, 4.9; N, 15.0. $C_{27}H_{23}N_5O_3$ requires C, 69.66; H, 4.98; N, 15.05%); ν_{max}(KBr)/cm^{-1} 3340 (NH_2), 3200 (NH), 2185 (CN) and 1720 (CO); δ_H(300 MHz, [$^2H_6$]DMSO) 2.73 (1 H, d) and 2.57 (1 H, d, $|^2J|$ 14.93, 3′-C*H*$_2$), 3.49 (3 H, s, OCH_3), 3.79 (3 H, s, OCH_3), 5.61 (2 H, s, NH_2), 6.29, 6.57, 6.73, 6.95, 7.17 and 7.20 (all m, 12 aryl-H) and 10.41 (1 H, s, NH); δ_C(75 MHz, [$^2H_6$]DMSO) 32.68 (C-3), 45.24 (C-3 = C-4′), 54.48 and 54.81 (O*C*H$_3$), 55.47 (C-5′), 109.31, 113.54, 114.28, 120.76, 121.63, 123.21, 128.23 and 130.30 (all aryl-*C*–H), 119.18 (*C*≡N), 129.16 (C-3a), 131.18 (C-7a), 140.56 and 140.93 (aryl-*C*–N), 152.78 (C-2′), 154.45 and 155.92 (aryl-*C*–OCH_3), 158.46 (C-6′) and 178.10 (C-2); *m*/*z* 465 (M^+, 6%), 270 (17), 195 (24), 168 (15), 148 (100), 140 (11), 123 (21), 107 (21), 92 (17), 77 (37) and 64 (12).

Crystal structure determination of compound 22b

A crystal was directly withdrawn from the mother liquor (chloroform).

Crystal data.† Siemens P4RA four circle diffractometer, rotating anode generator, Mo-Kα radiation (λ = 0.710 73 Å), graphite monochromator, scintillation counter, T = 150 K, empirical absorption corrections; SHELXTL-PLUS programs, $C_{30}H_{26}N_5OCl_9$, molecular weight 791.61, monoclinic, space group $P2_1/n$, a = 12.884(3), b = 14.206(3), c = 20.282(4) Å, β = 90.14(2)°, V = 3711.74 Å^3, Z = 4, D_x = 1.416 g cm^{-3}, μ(Mo-Kα) = 0.71 mm^{-1}, transmission range 0.764–0.685, crystal dimensions *ca.* 0.43 × 0.25 × 0.19 mm, ω-scan, $2\theta_{max}$ = 54°, 8122 unique reflections, direct methods, full-matrix least-squares refinement, $R(R_w)$ = 0.0597 (0.0571) for 5221 observed reflections with $I > 2\sigma(I)$, 438 variables, non-hydrogen atoms anisotropic, H-atoms at idealized positions, one common isotropic temperature factor for H within each residue, one extinction parameter, one scaling factor.

Acknowledgements

M. A. G. is deeply indebted to the Ministry of Higher Education of the A. R. of Egypt for being awarded a Ph.D. fellowship (1991–1993). Support of this work by Fonds der Chemischen Industrie is gratefully acknowledged.

† Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details of the CCDC deposition scheme, see 'Instructions for Authors (1996)', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1.

References

1 H. Aigner, H. Junek and H. Sterk, *Monatsh. Chem.*, 1970, **101**, 1145.
2 H. Junek, H. Aigner and H. Fischer-Colbrie, *Monatsh. Chem.*, 1972, **103**, 639.
3 H. Fischer-Colbrie, H. Aigner and H. Junek, *Monatsh. Chem.*, 1975, **106**, 743.
4 H. Junek, H. Fischer-Colbrie and H. Sterk, *Chem. Ber.*, 1977, **110**, 2276.
5 H. Sterk and H. Junek, *Tetrahedron*, 1970, **26**, 5361.
6 H. Junek, A. Hermetter, H. Fischer-Colbrie and H. Aigner, *Tetrahedron Lett.*, 1973, 2993.
7 R. Grigg and T. Mongkolaussavaratana, *J. Chem. Soc., Perkin Trans. 1*, 1988, 541.
8 Z. Rappoport and D. Ladkani, *J. Chem. Soc. B*, 1973, 1045.
9 H. R. Hirst and J. B. Cohen, *J. Chem. Soc.*, 1895, **67**, 829.
10 M. D. Farnow and C. K. Ingold, *J. Chem. Soc.*, 1924, **125**, 2543.
11 F. Benington, R. D. Morin and L. C. Clark, Jr., *J. Org. Chem.*, 1958, **23**, 19.
12 G. J. Ashwell, M. R. Bryce, S. R. Davies and M. Hasan, *J. Org. Chem.*, 1988, **53**, 4585.
13 M. R. Bryce, S. R. Davies, M. Hasan, G. J. Ashwell, M. Szablewski, M. G. B. Drew, R. Short and M. B. Hursthouse, *J. Chem. Soc., Perkin Trans. 2*, 1989, 1285.
14 A. J. Fatiadi, *Synthesis*, 1978, 165.
15 R. M. Roberts, *J. Org. Chem.*, 1949, **14**, 277.
16 E. C. Taylor and W. A. Erhart, *J. Org. Chem.*, 1963, **28**, 1108.

Paper 5/05904F
Received 6th September 1995
Accepted 1st November 1995