Alternative Synthesis of 6-(3-Methoxybenzyl)pyrazin-2(1*H*)-one. Synthesis of Indeno[1,2-*b*]pyrazin-2-ones. Crystal Structures of 5-Acetoxy-1-benzyl-4-*tert*-butoxycarbonyl-6-(3-methoxybenzylidene)piperazin-2-one, 1-Benzyl-4-*tert*-butoxycarbonyl-7-methoxy-1,3,4,4a-tetrahydroindeno[1,2-*b*]pyrazin-2-one and 1-Benzyl-4-*tert*-butoxycarbonyl-7-methoxy-1,3,4,9-tetrahydroindeno-[1,2-*b*]pyrazin-2-one

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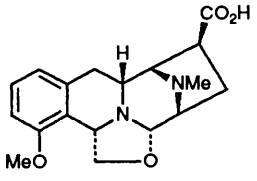
1-Acetyl-3-(3-methoxybenzylidene)piperazine-2,5-dione **7a** was converted *via* a 7-step sequence into 6-(3-methoxybenzyl)pyrazin-2(1*H*)-one **2a**. Treatment of 1-benzyl-4-*tert*-butoxycarbonyl-5-hydroxy-6-(3-methoxybenzylidene)piperazin-2-one **8a** with acids results in cyclisation to indeno-[1,2-*b*]pyrazin-2-ones, **9a**, **9b** or **11**. The X-ray crystal structure determinations of 5-acetoxy-1-benzyl-4-*tert*-butoxycarbonyl-6-(3-methoxybenzylidene)piperazin-2-one, **8b**, 1-benzyl-4-*tert*-butoxycarbonyl-7-methoxy-1,3,4,4a-tetrahydroindeno[1,2-*b*]pyrazin-2-one, **9b** and 1-benzyl-4-*tert*-butoxycarbonyl-7-methoxy-1,3,4,9-tetrahydroindeno[1,2-*b*]pyrazin-2-one, **11** are described.

There has been considerable interest in the development of synthetic routes[1] to the antitumour[2] metabolite quinocarcin **1**;[3] we and Garner[4] have utilised strategies in which the key 3,8-diazabicyclo[3.2.1]octane nucleus is constructed *via* a dipolar cycloaddition to a 3-oxidopyrazinium, though the methods employed for the generation of this are quite different. Garner has developed his route into a synthesis of quinocarcin itself in homochiral form.[5]



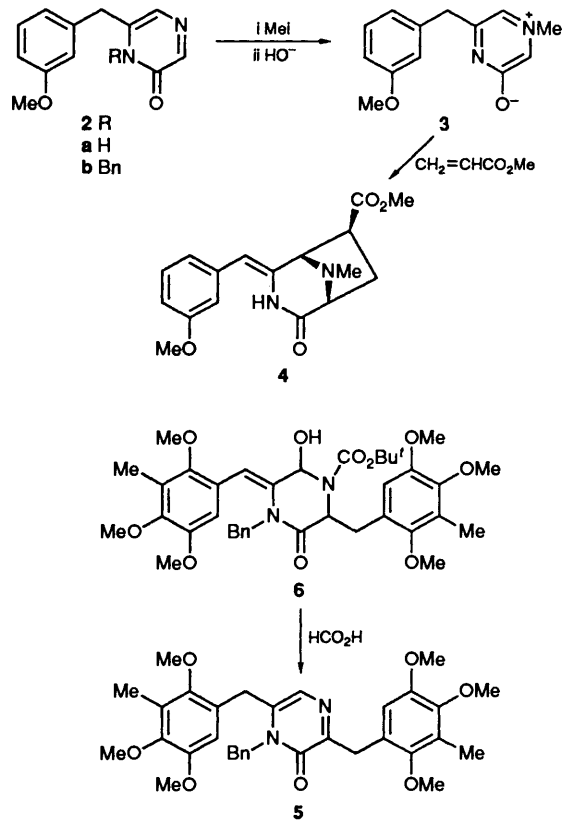
1

We showed that 1,5-dimethyl-3-oxidopyrazinium can be produced straightforwardly from 6-methylpyrazin-2-one *via* quaternisation then deprotonation, that the zwitterion is quite stable and easy to handle with few precautions, and readily undergoes dipolar cycloadditions, with the regiochemistry required for the construction of quinocarcin.[6] We subsequently developed a route to a 6-benzylpyrazin-2-one, **2a**, such as would be required for a synthesis of the natural product, and described its further development, *via* the corresponding oxidopyrazinium, **3**, into **4**,[7] which had been synthesised by Weinreb.[8] In this paper we discuss (a) an alternative, and potentially general route to benzylpyrazinones, (b) how intermediates in that route are converted into indeno[1,2-*b*]pyrazinones, and (c) the X-ray crystal structure determinations of a 6-benzylidenepyrazin-2-one and of two indeno[1,2-*b*]pyrazinones.

Prior to our report,[7] no 6-benzylpyrazin-2-ones were known. Kubo, in studies on the total synthesis of saframycin, had produced the 3,6-dibenzylpyrazin-2-one **5** by acid treatment of hemiamidal **6**.[9] The conversion must involve removal of the *N*-protecting group, loss of water and an isomerisation of the exocyclic double bond into the ring, presumably favoured by the formation of the aromatic pyrazinone unit. We set out to parallel this pyrazinone-forming process, aiming to adapt the strategy for a synthesis of a 6-benzylpyrazin-2-one, **2**.

The benzylidene-piperazine-dione **7a** was formed *via* the *tert*-butoxide catalysed aldol condensation between 3-methoxybenzaldehyde and 1,4-diacetylpiperazine-2,5-dione.[10] The geometry of **7a** was proved by the observation of an NOE between the alkene proton and aromatic protons and the absence of an NOE between this proton and the *N*-hydrogen. Spectroscopic comparisons and the X-ray structure determination of a derivative, **8b** (Fig. 1, see below), lead us to believe that **7b–e** also have *E* geometry.

After *N*-benzylation to give **7b**, the *N*-acetyl group was removed by hydrazinolysis, producing **7c** and formation of the corresponding urethane **7d** was achieved using di-*tert*-butyl



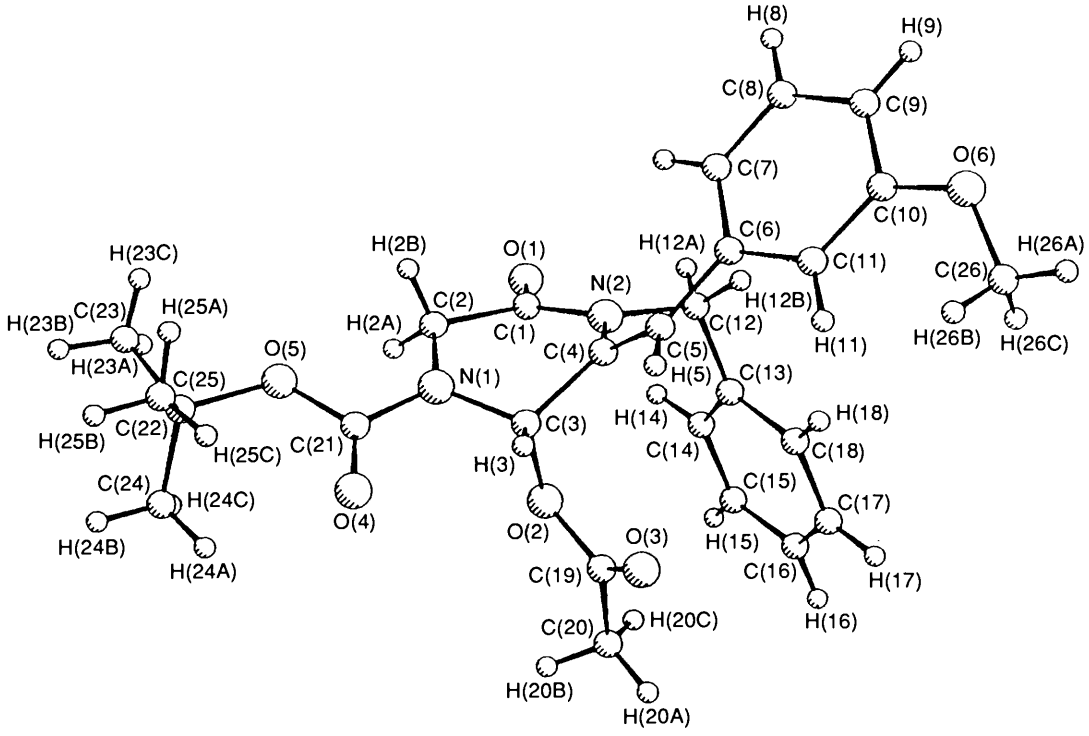
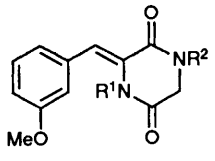


Fig. 1 PLUTO drawing of 5-acetoxy-1-benzyl-4-*tert*-butoxycarbonyl-6-(3-methoxybenzylidene)piperazin-2-one, **8b**

dicarbonate in the presence of 4-dimethylaminopyridine. This intermediate could also be obtained starting with 1,4-di-*tert*-butoxycarbonylpiperazine-2,5-dione, condensation with 3-methoxybenzaldehyde, which was only efficient using, as base, potassium fluoride on alumina,[11] giving **7e**, which on *N*-benzylation gave **7d**.

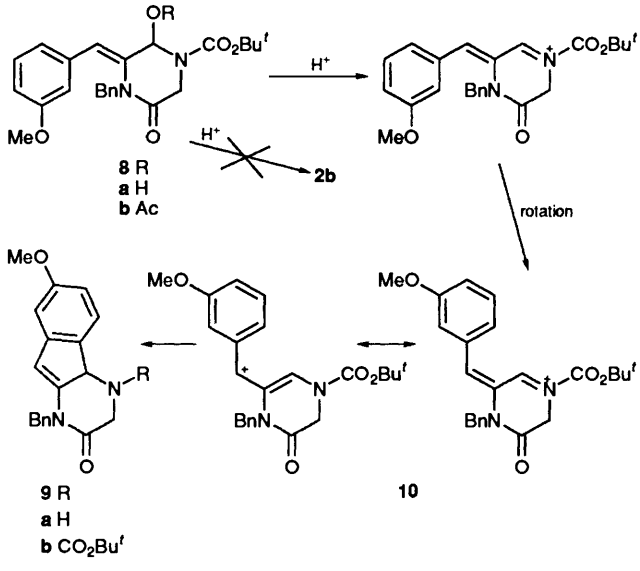


7	R^1	R^2
a	H	Ac
b	Bn	Ac
c	Bn	H
d	Bn	CO_2Bu^t
e	H	CO_2Bu^t

Selective reduction of the imide-type carbonyl in the ring was effected with lithium tri-*tert*-butoxyaluminium hydride at 0 °C producing a hemiamidal, **8a**. It was proposed that acid-catalysed *N*-deprotection of **8b**, then loss of water would lead to an intermediate requiring only double bond isomerisation to afford the pyrazinone, **2b**

When the hemiamidal **8a** was exposed to formic acid at room temperature a quantitative conversion into a new compound took place, but although it had clearly lost the urethane it was equally obvious that the product did not have the desired structure. Attempting the desired conversion using toluene-*p*-sulfonic acid, or even standing in deuteriochloroform solution, resulted once again in a virtually quantitative conversion taking place, into a product which resembled the first, save that it retained the *N*-*tert*-butoxycarbonyl substituent. Each product now had signals for only three aromatic protons, in addition to those for the benzyl substituent, together with an alkene singlet, δ 5.74 and 5.98, respectively, two methylene AB quartets and a one-hydrogen singlet, at δ 4.37 and 5.09, respectively. The tricyclic structures, **9a** and **9b** for the two products, were confirmed by crystallographic analysis of a sample of **9b** (Fig. 2).

In order to rationalise the formation of the indenopyrazinones there must be rotation of a nominal double bond in some intermediate, since a crystal structure determination of the



acetate **8b** of the hemiamidal showed the exocyclic double bond to have *Z* geometry which would not allow the observed closure; we speculate (shown for the formation of **9b**) that this rotation takes place in an acyliminium cation **10**, formed by proton-catalysed loss of water, and that the ring closure probably has the character of an electrophilic attack on the aromatic ring, though a 4π electrocyclic closure involving the five-atom cationic unit cannot be ruled out.

A third indenopyrazinone, **11** (Fig. 3), having the double bond endocyclic with respect to the pyrazinone ring, was formed when iodotrimethylsilane generated *in situ*[12] was employed in an attempt to remove[13] the *tert*-butoxycarbonyl group from **8a**. It was also shown that **9b** could be converted into its isomer **11** by exposure to iodotrimethylsilane, but that the latter was unaffected by exposure to toluene-*p*-sulfonic acid, the conditions used to form **9b**.

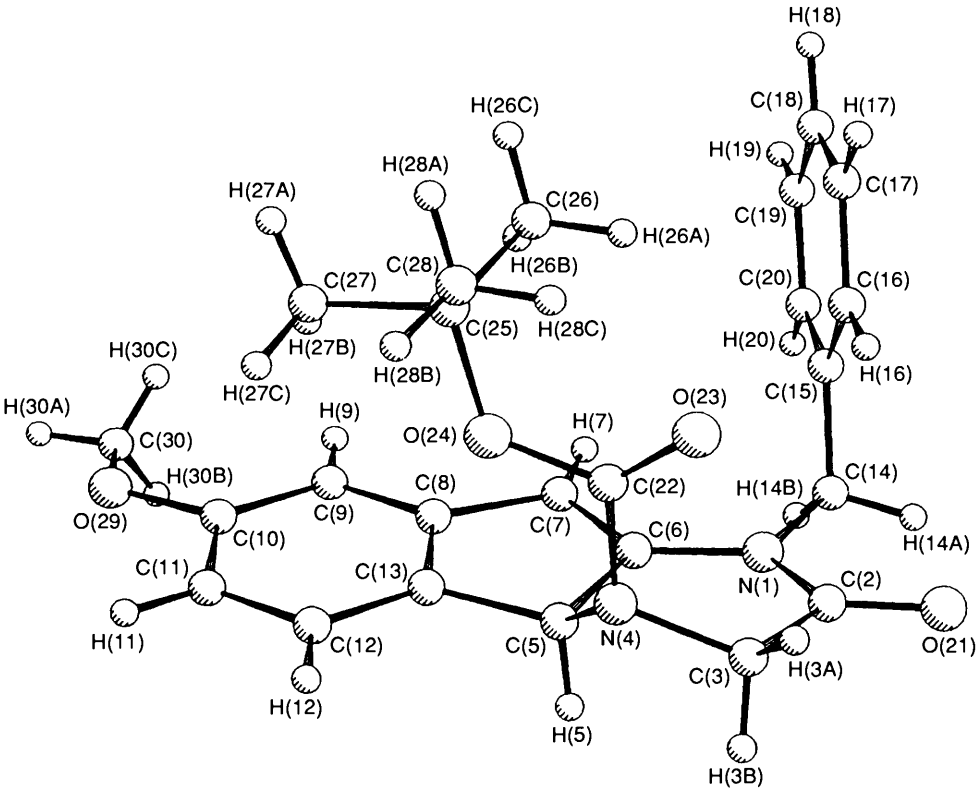
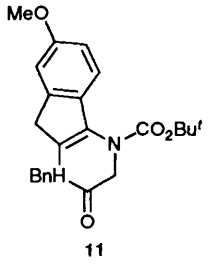
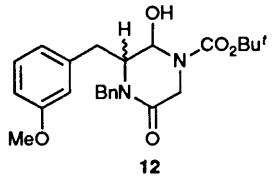


Fig. 2 PLUTO drawing of 1-benzyl-4-*tert*-butoxycarbonyl-7-methoxy-1,3,4,4a-tetrahydroindeno[1,2-*b*]pyrazin-2-one, **9b**



11



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Relatively few indenopyrazines have been previously described, and these were prepared by routes which do not parallel that described above, in that each started with a preformed indane or indene nucleus. Ninhydrin (2,2-dihydroxyindane-1,3-dione) and indane-1,2-dione,[14] have been condensed with 1,2-dicyanoethene-1,2-diamine[15] and α-amino acid amides,[16] the former with ethane-1,2-diamine,[17] and indane-1,2-dione 2-oxime with α-aminonitriles[18] to afford the ring system. Construction of the pyrazine ring using indene-1,2-diamine[19] and indane-1,2-diamine[20] derivatives has also been employed to give indeno[1,2-*b*]pyrazines.

Returning to the problem of transforming hemiamidal **8a** into a 6-benzylpyrazin-2-one, the exocyclic double bond was removed by catalytic hydrogenation forming **12**. Now, on *N*-deprotection with formic acid in the presence of air, no ring closure was observed, the desired transformation could be achieved and **2b** formed in high yield, presumably *via* a dihydro-species which was aerially oxidised. Finally, conversion into the previously obtained 6-(3-methoxybenzyl)pyrazin-2(1*H*)-one **2a** was effected by debenzylation[21] using sodium in liquid ammonia.

Experimental

General.—Thin-layer chromatography was carried out on Merck silica gel F_{254} 0.255 mm plates, and spots were visualised, where appropriate, by spraying with potassium permanganate solution or acidified cerium sulfate solution. Column chromatography was performed using Merck Kieselgel (60) (230–400 mesh) silica. Organic solutions were dried over dried magnesium sulfate. Tetrahydrofuran was dried by distillation from sodium–benzophenone; toluene and triethylamine were dried by distillation from calcium hydride; dimethylformamide was dried over 4 Å molecular sieves; dichloromethane was dried by distillation from calcium hydride. Light petroleum refers to the fraction with boiling range 40–60 °C. UV spectra were recorded on a Shimadzu U.V. 260 UV–VIS recording spectrophotometer at fast scan speed, path length 1 cm. IR spectra were recorded on a Perkin-Elmer 1710 Infra Red Fourier transform spectrometer. ^{1}H NMR spectra were recorded on a Varian AC 300E NMR spectrometer at 300 MHz or a Varian Gemini 200 spectrometer operating at 200 MHz. Peak multiplicities are denoted by s (singlet), br s (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or by a combination of these *e.g.* dd (double doublet), with coupling constants (J) given in Hz. ^{13}C NMR spectra were recorded on a Varian AC 300E NMR spectrometer at 75 MHz. Mass spectra were recorded on a Kratos MS 25 for the electron impact (EI) and chemical ionisations (CI). In the latter case ammonia was used as the ionising reagent. Accurate mass measurements were recorded on a Kratos Concept. All reactions were carried out under a dry atmosphere of argon or nitrogen unless otherwise stated.

1,4-*Diacetylpiperazine*-2,5-*dione.*—Piperazine-2,5-dione (11.4 g, 100 mmol) was refluxed in acetic anhydride (50 cm^3) for 7 h, then the solvent was evaporated under reduced pressure and the crude solid product recrystallised from ethyl acetate–hexane to give the title compound as a white solid (17.4 g, 88%, m.p. 98–100 °C, lit.,[22] 99.5–100.5 °C), ν_{max}(film)/cm^{-1} 1711; δ_H($CDCl_3$) 4.65 (4 H, s, 2 × CH_2) and 2.60 (6 H, s, 2 × CH_3); m/z (EI, %) 198 (M^+, 39), 170 (88), 156 (52), 114 (75) and 43 (100).

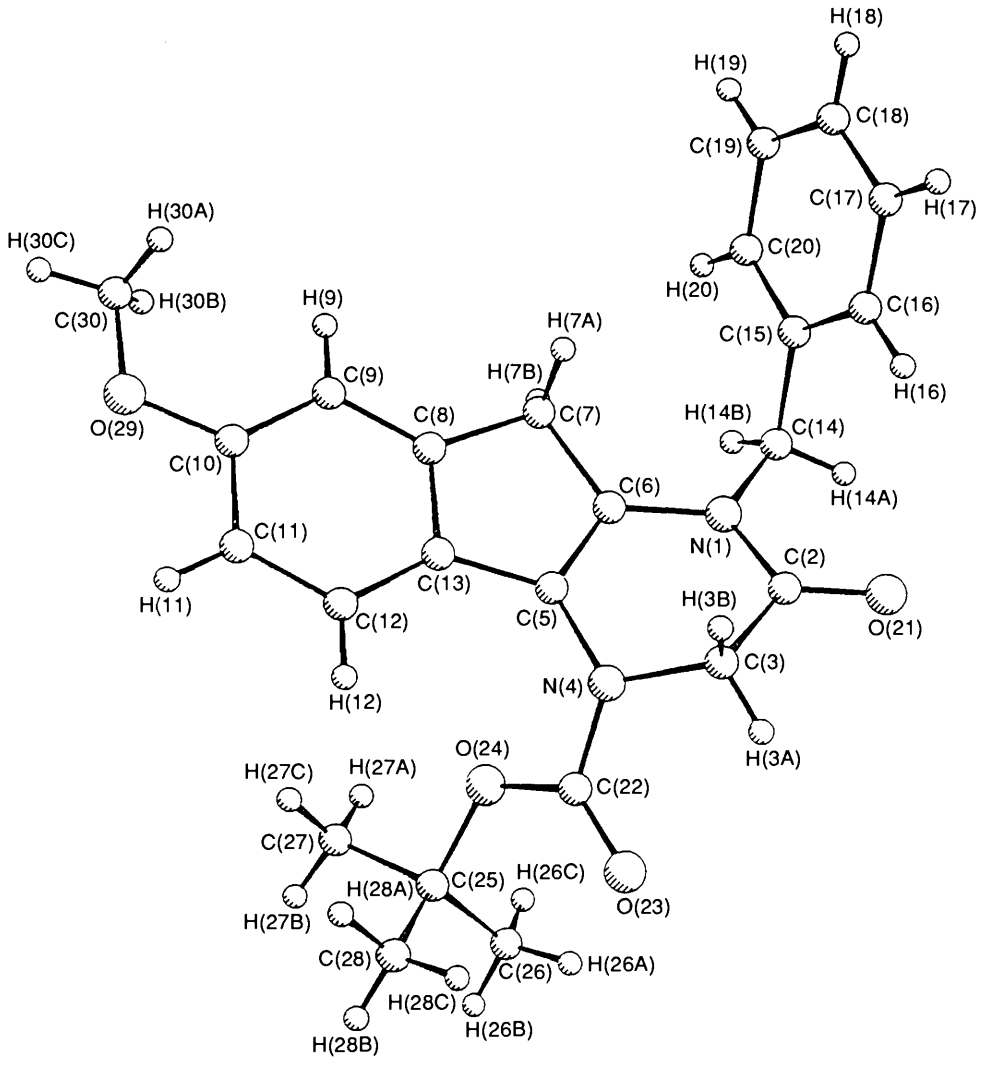

Fig. 3 PLUTO drawing of 1-benzyl-4-*tert*-butoxycarbonyl-7-methoxy-1,3,4,9-tetrahydroindeno[1,2-*b*]pyrazin-2-one, **11**

1-*Acetyl*-3-(3-*methoxybenzylidene*)*piperazine*-2,5-*dione*, **7a**.—1,4-Diacetylpiperazine-2,5-dione (11.7 g, 59 mmol) and *m*-anisaldehyde (32.64 g, 240 mmol) were stirred in DMF (*N*,*N*-dimethylformamide) (120 cm^3) under nitrogen at 0 °C and to this solution was added potassium *tert*-butoxide (6.61 g, 59 mmol) in *tert*-butyl alcohol (118 cm^3) over 20 min. After stirring at room temp. for 6 h the solution was neutralised with acetic acid and poured into water (300 cm^3). This aqueous solution was extracted with chloroform (3 × 200 cm^3) and the combined organic extracts were dried, concentrated under reduced pressure and the crude solid product recrystallised from ethyl acetate–methanol to give the *condensation product*, **7a**, as a white solid (10.14 g, 63%), m.p. 198–200 °C, λ_{max}(EtOH)/nm (log ε) 316 (2.93) and 204 (3.20); ν_{max}(film)/cm^{-1} 2924, 1691 and 1628; δ_H($CDCl_3$) 7.95 (1 H, br s, NH), 7.39 (1 H, t, *J* 8, ArH), 7.15 (1 H, s, C=CH), 7.00–6.85 (3 H, m, ArH), 4.53 (2 H, s, CH_2), 3.85 (3 H, s, OCH_3) and 2.67 (3 H, s, CH_3); *m*/*z* (EI, %) 274 (100, M^+), 232 (79) and 147 (71) (Found: C, 61.2; H, 5.1; N, 10.2. $C_{14}H_{14}N_2O_4$ requires C, 61.3; H, 5.1; N, 10.2%).

1-*Acetyl*-4-*benzyl*-3-(3-*methoxybenzylidene*)*piperazine*-2,5-*dione*, **7b**.—Sodium hydride (80% oil dispersion washed with dry hexane 3 times, 0.63 g, 26.3 mmol) was added to a stirred solution of 1-acetyl-3-(3-methoxybenzylidene)piperazine-2,5-dione (7.0 g, 25.5 mmol) in DMF (150 cm^3) at 0 °C. Stirring was continued at this temperature for 30 min and then benzyl bromide (3.05 cm^3, 25.7 mmol) in DMF (30 cm^3) was added dropwise over 10 min. The reaction mixture was allowed to warm to room temp. and then stirred for a further 2 h, after which time the solution was concentrated and the residue extracted from water (50 cm^3) with chloroform (3 × 75 cm^3). The combined organic extracts were dried and concentrated and the crude product recrystallised from toluene to give the N-*benzylpiperazinedione*, **7b**, as a white solid (7.62 g, 82%), m.p. 123–124 °C, λ_{max}(95% EtOH)/nm (log ε) 315 (3.91) and 208 (4.24); ν_{max}(film)/cm^{-1} 3030, 2957, 1690 and 1630; δ_H($CDCl_3$) 7.10–7.45 (5 H, m, ArH and C=CH), 6.80–7.05 (5 H, m, ArH), 4.65 (2 H, s, $PhCH_2N$), 4.52 (2 H, s, CH_2), 3.82 (3 H, s, OCH_3) and 2.52 (3 H, s, CH_3); *m*/*z* (EI, %) 364 (M^+, 95), 231 (41) and 91 (100) (Found: C, 69.2; H, 5.6; N, 7.7. $C_{21}H_{20}N_2O_4$ requires C, 69.2; H, 5.5; N, 7.7%).

4-*Benzyl*-3-(3-*methoxybenzylidene*)*piperazine*-2,5-*dione*, **7c**.—To a stirred solution of 1-acetyl-4-benzyl-3-(3-methoxybenzylidene)piperazine-2,5-dione **7b** (5.43 g, 14.9 mmol) in DMF (100 cm^3) at room temperature was added hydrazine monohydrate (0.92 cm^3, 19.1 mmol). The resulting solution was stirred for 1 h and then concentrated and organic material extracted from water (50 cm^3) with chloroform (3 × 100 cm^3). The chloroform extracts were dried and concentrated and the crude product recrystallised from ethyl acetate to give the *piperazine-dione*, **7c**, as a white solid (4.24 g, 88%), m.p. 168–170 °C, λ_{max}(95% EtOH)/nm (log ε) 294 (3.92) and 206 (4.17); ν_{max}(film)/cm^{-1} 3230, 1692 and 1631; δ_H($CDCl_3$) 7.10–7.40 (5 H, ArH and

C=CH), 6.82–7.00 (5 H, ArH), 6.15 (1 H, br s, NH), 4.72 (2 H, s, $PhCH_2N$), 4.13 (2 H, d, *J* 2.3, CH_2) and 3.83 (3 H, s, OCH_3); *m/z* (EI, %) 322 (M^+, 21), 231 (13) and 91 (100) (Found: C, 70.5; H, 5.7; N, 8.7. $C_{19}H_{18}N_2O_3$ requires C, 70.8; H, 5.6; N, 8.7%).

1,4-*Di*-tert-*butoxycarbonylpiperazine*-2,5-*dione*.—To piperazine-2,5-dione (1.0 g, 8.8 mmol), triethylamine (5.0 cm^3, 35.5 mmol) and 4-dimethylaminopyridine (4.3 g, 34.7 mmol) in pyridine (50 cm^3) at 0 °C was added dropwise over 10 min di-*tert*-butyl dicarbonate (7.7 g, 39.7 mmol). The solution was stirred at 60 °C for 12 h and then poured into dichloromethane (100 cm^3) and extracted with 3 mol dm^{-3} hydrochloric acid (210 cm^3). The organic extracts were dried and concentrated and the resultant oil purified by column chromatography (1:1 ethyl acetate–diethyl ether) to give a pale brown solid which was recrystallised from ethyl acetate–light petroleum (b.p. 60–80 °C) to give 1,4-*di*-tert-*butoxycarbonylpiperazine*-2,5-*dione* as a white solid (594 mg, 22%), m.p. 135–137 °C, ν_{max}(film)/cm^{-1} 2982, 1782 and 1731; δ_H($CDCl_3$) 4.37 (4 H, s, 2 × CH_2) and 1.47 [18 H, s, 2 × $C(CH_3)_3$]; *m/z* (EI, %) 215 (13), 159 (68), 115 (79) and 56 (100) (Found: M^+, 314.1470. $C_{14}H_{22}N_2O_6$ requires *M*, 314.1478).

1-tert-*Butoxycarbonyl*-3-(3-*methoxybenzylidene*)*piperazine*-2,5-*dione*, **7e**.—Potassium fluoride (5 g, 0.087 mmol) and alumina (6.7 g, 0.067 mmol) were shaken together in water (60 cm^3) and then the water was evaporated and the solid residue dried under reduced pressure at 70 °C for 8 h. Potassium fluoride–alumina (1.2 g), 1,4-di-*tert*-butoxycarbonylpiperazine-2,5-dione (500 mg, 1.6 mmol) and *m*-anisaldehyde (220 mg, 1.62 mmol) were shaken together in ethyl acetate (15 cm^3). The solvent was then evaporated and the solid residue irradiated under microwaves in a 240 W oven for 15 min in an open flask. After cooling to room temp. the solid was extracted with DMF (2 × 50 cm^3) and the solution then concentrated and the resultant pale yellow oil purified by column chromatography (ethyl acetate). This gave rise to a pale yellow solid which was then recrystallised from ethyl acetate to give the title compound as a white solid (340 mg, 64%), m.p. 98–100 °C, λ_{max}(95% EtOH)/nm (log ε) 311 (4.14), 219sh (4.17) and 204 (4.27); ν_{max}(film)/cm^{-1} 2981, 1775, 1703 and 1636; δ_H($CDCl_3$) 7.99 (1 H, br s, NH), 7.35 (1 H, t, *J* 7.8, ArH), 7.13 (1 H, s, C=CH), 6.90 (3 H, m, ArH), 4.45 (2 H, s, CH_2), 3.82 (3 H, s, OCH_3) and 1.59 [9 H, s, $C(CH_3)_3$]; *m/z* (EI, %) 233 (40) and 30 (100) (Found: M^+, 332.1372. $C_{17}H_{20}N_2O_5$ requires *M*, 332.1372).

4-*Benzyl*-1-tert-*butoxycarbonyl*-3-(3-*methoxybenzylidene*)-*piperazine*-2,5-*dione*, **7d**.—(a) To 4-benzyl-3-(3-methoxybenzylidene)piperazine-2,5-dione **7c** (2.38 g, 7.4 mmol), triethylamine (2.07 cm^3, 14.7 mmol) and 4-dimethylaminopyridine (1.82 g, 14.7 mmol) in dichloromethane (75 cm^3) at 0 °C was added dropwise over 10 min di-*tert*-butyl dicarbonate (6.48 g, 29.5 mmol). The solution was stirred at room temp. for 1 h and then washed with 1 mol dm^{-3} hydrochloric acid (2 × 10 cm^3), dried and concentrated. The solid residue was then recrystallised from ethyl acetate–light petroleum (60–80 °C) to give the *piperazine-dione*, **7d**, as a white solid (2.84 g, 88%), m.p. 119–120 °C, λ_{max}(95% EtOH)/nm (log ε) 311 (4.05) and 209 (4.35); ν_{max}(film)/cm^{-1} 2980, 1725, 1697 and 1630; δ_H($CDCl_3$) 7.10–7.40 (5 H, ArH), 6.80–7.00 (5 H, ArH and C=CH), 4.64 (2 H, s, $PhCH_2$), 4.37 (2 H, s, CH_2), 3.80 (3 H, s, OCH_3) and 1.53 [9 H, s, $C(CH_3)_3$]; *m/z* (EI, %) 323 (100), 233 (25) and 91 (25) (Found: C, 68.2; H, 6.1; N, 6.7. $C_{24}H_{26}N_2O_5$ requires C, 68.3; H, 6.2; N, 6.6%). (b) Sodium hydride (80% oil dispersion washed with dry hexane 3 times, 6 mg, 0.2 mmol) was added to a solution of 1-*tert*-butoxycarbonyl-3-(3-methoxybenzylidene)piperazine-2,5-dione **7e** (55.4 mg, 0.17 mmol) in DMF (5 cm^3) at 0 °C. The solution was then stirred at the same temperature for 30 min and then benzyl bromide (0.02 cm^3, 0.17 mmol) in DMF (4 cm^3) was added dropwise over 10 min. The solution was allowed to warm to room temp. and was then stirred for a further 2 h. The solvent was then evaporated and the residue extracted from water (10 cm^3) with chloroform (3 × 10 cm^3). The organic extracts were dried and concentrated and the resultant oil recrystallised from ethyl acetate–hexane to give the title compound as a white solid (65.1 mg, 92%), shown to be identical by thin-layer chromatography, m.p. and spectroscopic properties to material prepared by method (a).

1-*Benzyl*-4-tert-*butoxycarbonyl*-5-*hydroxy*-6-(3-*methoxybenzylidene*)*piperazin*-2-*one*, **8a**.—To a stirred solution of 4-benzyl-1-*tert*-butoxycarbonyl-3-(3-methoxybenzylidene)piperazine-2,5-dione **7d** (1.0 g, 2.36 mmol) in THF (75 cm^3) at 0 °C was added lithium tri-*tert*-butoxyaluminiumhydride (3.3 cm^3 of a 1 mol dm^{-3} solution in hexane, 3.3 mmol) over 30 min. The solution was then stirred at 0 °C for a further hour and then water (5 cm^3) in THF (25 cm^3) was added slowly to quench the reaction. The solution was then filtered through Celite and concentrated and the residue extracted from water (25 cm^3) with chloroform (3 × 75 cm^3). The combined organic extracts were then concentrated and the crude oil purified by column chromatography (2:1 diethyl ether–hexane) to give the product as a white foam, which on recrystallisation from ethyl acetate–hexane gave the *hemiamidal*, **8a**, as a white solid (667 mg, 66%), m.p. 122–125 °C, λ_{max}(95% EtOH)/nm (log ε) 264 (4.14) and 209 (4.39); ν_{max}(film)/cm^{-1} 3403, 2977, 1698 and 1652; δ_H($CDCl_3$) 6.75–7.4 (9 H, ArH), 6.40 (1 H, br s, C=CH), 5.75 (1 H, br s, NCHO), 4.62 (2 H, AB q, *J* 16.2, $PhCH_2N$), 4.22 (2 H, AB q, *J* 16.9, CH_2), 3.85 (3 H, s, OCH_3), 3.18 (1 H, br s, OH) and 1.55 [9 H, s, $C(CH_3)_3$]; *m/z* (CI, %) 425 (MH^+, 10), 369 (43), 325 (30), 307 (100) and 91 (59) (Found: C, 67.7; H, 6.6; N, 6.8. $C_{24}H_{28}N_2O_5$ requires C, 67.8; H, 6.6; N, 6.6%).

1-*Benzyl*-7-*methoxy*-1,3,4,4*a*-*tetrahydroindeno*[1,2-b]*pyrazin*-2-*one*, **9a**.—1-Benzyl-4-*tert*-butoxycarbonyl-5-hydroxy-6-(3-methoxybenzylidene)piperazin-2-one **8a** (100 mg, 0.24 mmol) was stirred in formic acid (5 cm^3) for 1 h, then the solution was neutralised with saturated sodium hydrogen carbonate solution and extracted with dichloromethane (3 × 10 cm^3). The combined organic extracts were concentrated to give the spectroscopically pure *indenopyrazinone*, **9a**, as a pale yellow solid (72.1 mg, 100%), recrystallisation from methanol giving analytically pure pale yellow needles, m.p. 181–182 °C, λ_{max}(95% EtOH)/nm (log ε) 300 (4.00), 243 (4.29) and 204 (4.32); ν_{max}(film)/cm^{-1} 2925, 1677 and 1609; δ_H($CDCl_3$) 7.31 (6 H, m, ArH), 6.68 (1 H, d, *J* 2.2, ArH), 6.60 (1 H, dd, *J* 2.4, 8.1, ArH), 5.74 (1 H, s, C=CH), 4.96 (2 H, AB q, *J* 15.3, $PhCH_2N$), 4.37 (1 H, s, CHN), 3.90 (2 H, AB q, *J* 14, CH_2) and 3.78 (3 H, s, OCH_3); δ_C($CDCl_3$) 167.2, 160.7, 149.9, 145.4, 136.3, 130.4, 128.9, 127.8, 127.6, 123.9, 108.9, 107.1, 104.9, 61.1, 55.6, 50.3 and 46.6; *m/z* (CI, %) 307 (MH^+, 100%), 215 (84) and 91 (27) (Found: C, 74.2; H, 5.9; N, 9.1. $C_{19}H_{18}N_2O_2$ requires C, 74.5; H, 5.9; N, 9.2%).

1-*Benzyl*-4-tert-*butoxycarbonyl*-7-*methoxy*-1,3,4,4*a*-*tetrahydroindeno*[1,2-b]*pyrazin*-2-*one*, **9b**.—1-Benzyl-4-*tert*-butoxycarbonyl-5-hydroxy-6-(3-methoxybenzylidene)piperazin-2-one **8a** (70 mg, 0.17 mmol) was stirred with toluene-*p*-sulfonic acid (300 mg, 1.6 mmol) in toluene (10 cm^3) at room temp. for 30 min. The solution was then basified with saturated aqueous sodium carbonate and extracted with ethyl acetate (3 × 10 cm^3). The combined organic extracts were then dried and concentrated to give the spectroscopically pure *indenopyrazinone*, **9b**, as a pale brown oil (67 mg, 100%). Recrystallisation from ethyl acetate–light petroleum gave pale yellow flakes, m.p. 119–120 °C, λ_{max}(95% EtOH)/nm (log ε) 310 (3.91), 242 (4.16) and

209 (4.26); ν_{max}(film)/cm^{-1} 2978, 1695 and 1613; δ_H($CDCl_3$) 7.30 (6 H, m, ArH), 6.69 (1 H, d, *J* 2.3, ArH), 6.66 (1 H, dd, *J* 2.4 and 8.2, ArH), 5.98 (1 H, d, *J* 1.5, C=CH), 5.09 (1 H, m, CHN), 4.97 (2 H, br s, $PhCH_2N$), 4.30 (2 H, q, *J* 16.6, CH_2), 3.78 (3 H, s, OCH_3) and 1.41 [9 H, s, $C(CH_3)_3$]; *m/z* (CI, %) 424 (MNH_4^+, 26), 407 (MH^+, 16), 368 (100), 351 (49), 307 (68) and 91 (29) (Found: C, 71.2; H, 7.3; N, 7.1. $C_{24}H_{26}N_2O_4$ requires C, 70.9; H, 7.3; N, 6.9%).

1-*Benzyl*-4-tert-*butoxycarbonyl*-5-*hydroxy*-6-(3-*methoxybenzyl*)*piperazin*-2-*one*, **12**.—1-Benzyl-4-*tert*-butoxycarbonyl-5-hydroxy-6-(3-methoxybenzylidene)piperazin-2-one **8a** (2.80 g, 6.60 mmol) was shaken with 10% palladium on carbon catalyst (1.0 g) in absolute ethanol (60 cm^3) under 4 atmospheres of hydrogen for 24 h. The solution was then filtered through Celite and the residue washed with ethyl acetate (100 cm^3). The solvent was then evaporated and the crude product recrystallised from ethyl acetate–hexane to give the title compound as a white solid (2.10 g, 75%), m.p. 152–154 °C, ν_{max}(film)/cm^{-1} 3368, 2931, 1704 and 1639; δ_H($CDCl_3$) 7.1–7.4 (5 H, ArH), 7.20 (1 H, t, *J* 7.0, ArH), 6.78 (1 H, d, *J* 7.0, ArH), 6.64 (1 H, d, *J* 7.0, ArH), 6.58 (1 H, s, ArH), 5.55 (1 H, br s, OCHN), 5.21 (1 H, d, *J* 14.9, one of ring-CH_2), 4.06–4.00 (3 H, m, one of ring-CH_2 and $PhCH_2N$), 3.77 (3 H, s, OCH_3), 3.55 (1 H, m, $ArCH_2CH$), 2.70 (2 H, m, $ArCH_2$) and 1.48 [9 H, s, $C(CH_3)_3$]; *m/z* (CI, %) 427 (MH^+, 55), 309 (50), 91 (100) (Found: C, 67.6; H, 7.2; N, 6.8. $C_{24}H_{30}N_2O_5$ requires C, 67.6; H, 7.0; N, 6.6%).

5-*Acetoxy*-1-*benzyl*-4-tert-*butoxycarbonyl*-6-(3-*methoxybenzylidene*)*piperazin*-2-*one*, **8b**.—1-Benzyl-4-*tert*-butoxycarbonyl-5-hydroxy-6-(3-methoxybenzylidene)piperazin-2-one **8a** (200 mg, 0.47 mmol), triethylamine (0.50 cm^3, 3.75 mmol) and acetic anhydride (380 mg, 0.35 cm^3, 3.75 mmol) were stirred together for 18 h at room temp. After this time TLC analysis showed only one product. The solvent was evaporated to give a crude brown oil (212 mg) which by TLC analysis was a mixture of four compounds; product, starting material, indeno[1,2-*b*]pyrazin-2-one, **9b** and one other. Two recrystallisations from ethyl acetate–hexane gave the *acetate*, **8b**, as colourless acicular crystals (64.8 mg, 29%), m.p. 142–144 °C, ν_{max}(film)/cm^{-1} 2977, 1714, 1690 and 1656; δ_H(CD_3OD) 7.45 (1 H, t, *J* 8.0, ArH), 7.35 (3 H, m, ArH), 7.05 (4 H, m, ArH), 7.00 (1 H, s, ArH), 6.35 (1 H, s, C=CH), 5.53 (0.5 H, s, NCHOAc), 5.45 (0.5 H, s, NCHOAc), 5.35 (1 H, d, *J* 14.5, one of ring-CH_2), 4.45 (1 H, t, *J* 18, CH_2), 4.20 (1 H, d, *J* 14.5, one of ring-CH_2), 4.12 (1 H, m, $PhCH_2N$), 3.90 (3 H, s, OCH_3), 2.10 (3 H, s, CH_3) and 1.60 [9 H, s, $C(CH_3)_3$], *m/z* (FAB, %) 466 (M^+, 10), 407 (33), 351 (95), 307 (71), 91 (100) (Found: C, 67.2; H, 6.6; N, 6.1. $C_{26}H_{30}N_2O_6$ requires C, 67.0; H, 6.4; N, 6.0%).

1-*Benzyl*-4-tert-*butoxycarbonyl*-7-*methoxy*-1,3,4,9-*tetrahydroindeno*[1,2-b]*pyrazin*-2-*one*, **11**.—(a) A mixture of sodium iodide (90 mg, 0.60 mmol) and chlorotrimethylsilane (65 mg, 0.60 mmol, 0.075 cm^3) was stirred in acetonitrile (5 cm^3) at room temp. for 15 min. A solution of 1-benzyl-4-*tert*-butoxycarbonyl-5-hydroxy-6-(3-methoxybenzylidene)pyrazin-2-one **8a** (212 mg, 0.50 mmol) in acetonitrile (10 cm^3) was then added, and stirring continued at room temp. for 20 min. The reaction was then quenched with methanol (2.0 cm^3) and the solvent evaporated. The residue was then partitioned between water (10 cm^3) and dichloromethane (10 cm^3). The layers were separated and the aqueous layer extracted with dichloromethane (2 × 10 cm^3). The combined organic extracts were dried and concentrated and purified by column chromatography (diethyl ether–light petroleum, 1 : 1 eluent) to give the title compound as a pale brown powder (63 mg, 31%). Recrystallisation from methanol gave pink plates, m.p. 188–190 °C, ν_{max}(film)/cm^{-1} 2979 and 1681; δ_H($CDCl_3$) 7.18 (6 H, m, ArH), 6.85 (1 H, d, *J* 2.1, ArH), 6.80 (1 H, dd, *J* 1.3 and 8.2, ArH), 4.94 (1 H, s, $PhCH_2N$), 4.49 (2 H, s, $ArCH_2N$), 3.79 (3 H, s, OCH_3), 3.34 (2 H, s, CH_2) and 1.53 [9 H, s, $C(CH_3)_3$]; *m/z* (EI, %) 406 (M^+, 10), 350 (21), 306 (18), 259 (21), 215 (20), 187 (20) and 91 (100) (Found: C, 69.9; H, 6.4; N, 6.5. $C_{24}H_{26}N_2O_4$ requires C, 70.9%; H, 6.4; N, 6.9%). (b) A mixture of sodium iodide (22 mg, 0.15 mmol) and chlorotrimethylsilane (16 mg, 0.14 mmol, 0.018 cm^3) was stirred in acetonitrile (1 cm^3) at room temp. for 15 min. A solution of 1-benzyl-4-*tert*-butoxycarbonyl-7-methoxy-1,3,4,4a-tetrahydroindeno[1,2-*b*]pyrazin-2-one, **9b** (48 mg, 0.12 mmol) in acetonitrile (2 cm^3) was then added, and stirring continued at room temp. for 20 min. The reaction was then quenched with methanol (0.5 cm^3) and the solvent evaporated. The residue was then partitioned between water (10 cm^3) and dichloromethane (10 cm^3). The layers were separated and the aqueous layer extracted with dichloromethane (2 × 10 cm^3). The combined organic extracts were dried and concentrated and purified by column chromatography (ethyl acetate eluent) to give the title compound as a pale brown oil (16 mg, 33%), having identical spectroscopic properties to those quoted above.

1-*Benzyl*-6-(3-*methoxybenzyl*)*pyrazin*-2(1H)-*one*, **2b**.—Compressed air was bubbled through a stirred solution of 1-benzyl-4-*tert*-butoxycarbonyl-5-hydroxy-6-(3-methoxybenzyl)piperazine-2-one **12** (50 mg, 0.12 mmol) in formic acid (10 cm^3) at 60 °C for 4 h. The solution was neutralised with saturated sodium hydrogen carbonate solution and extracted with dichloromethane (3 × 20 cm^3). The combined organic extracts were dried, concentrated and purified by column chromatography (diethyl ether) to give the title compound as a pale brown oil (26.7 mg, 74%), ν_{max}(film)/cm^{-1} 2940, 1664 and 1583; δ_H($CDCl_3$) 8.20 (1 H, s, pyrazinone-3-H), 7.10–7.40 (7 H, m, pyrazinone-5-H and ArH), 6.84 (1 H, dd, *J* 2.6 and 8.1, ArH), 6.60–6.71 (2 H, m, ArH), 5.15 (2 H, s, $PhCH_2N$), 3.82 (2 H, s, $ArCH_2$) and 3.79 (3 H, s, OCH_3); *m/z* (EI, %) 306 (M^+, 14), 215 (30) and 91 (100) (Found: M^+, 306.1359. $C_{19}H_{18}N_2O_2$ requires *M*, 306.1368).

6-(3-*Methoxybenzyl*)*pyrazin*-2(1H)-*one*, **2a**.—Liquid ammonia (5 cm^3) was condensed using a cold finger into a solution of 1-benzyl-6-(3-methoxybenzyl)pyrazin-2-one **2b** (61.3 mg, 0.20 mmol) in tetrahydrofuran (2 cm^3) then sodium was added in small pieces until a blue colour had developed. The solution was then quenched with ammonium chloride and the ammonia allowed to evaporate. The solution was then concentrated and the residue partitioned between water (10 cm^3) and dichloromethane (10 cm^3). The layers were separated and the aqueous layer extracted with dichloromethane (2 × 10 cm^3). The combined organic extracts were dried and concentrated and the residual yellow-brown oil purified by column chromatography (ethyl acetate) to give the title compound as a pale yellow oil (21.4 mg, 49%), ν_{max}(film)/cm^{-1} 2938, 1657, 1601 and 1491; δ_H($CDCl_3$) 12.40 (1 H, s, NH), 8.05 (1 H, s, pyrazinone-3-H), 7.32 (1 H, s, pyrazinone-5-H), 7.25 (1 H, t, *J* 8.1, ArH), 6.85 (3 H, m, ArH), 3.84 (2 H, s, CH_2) and 3.79 (3 H, s, OCH_3); *m/z* (EI, %) 216 (100), 215 (36), 121 (30) and 91 (31) (Found: M^+, 216.0896. $C_{12}H_{12}N_2O_2$ requires *M*, 216.0899).

X-Ray Structure Determinations of Compounds **8b**, **9b** *and* **11**.—Intensity data were collected using Rigaku AFC5R (Cu-Kα) for **8b** and **9b** and for **11**, Rigaku AFC6S (Mo-Kα) diffractometers. Neutral atom scattering factors were taken from Cromer and Waber.[23] Anomalous dispersion effects were included in F_{calc}.[24] Values for $\Delta f'$ and $\Delta f''$ were those of Cromer.[25] All calculations were performed using the TEXSAN[26] crystallographic software package of Molecular Structure Corporation.

5-*Acetoxy*-1-*benzyl*-4-tert-*butoxycarbonyl*-6-(3-*methoxybenzylidene*)*piperazin*-2-*one*, **8b**.—*Crystal data*. $C_{26}H_{30}N_2O_6$, M = 466.53, monoclinic, a = 9.585(1), b = 12.644(6), c = 21.612(3) Å; β = 101.91(1)°; U = 2563 Å^3, Z = 4, ρ_c = 1.209, μ(Cu-Kα) = 6.71 cm^{-1}, space group $P2_1/n$ (# 14), 1350 unique reflections with $I > 3\sigma(I)$, R = 7.4%.

A colourless acicular crystal, approximately 0.06 × 0.10 × 0.38 mm was mounted on a glass fibre for measurements. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully-centred reflections in the range 32.99 < 2θ < 48.44° corresponded to a monoclinic cell. Data were collected at 21 ± 1 °C using the $\omega/2\theta$ scanning technique to a maximum 2θ value of 120.2°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.29° with a take-off angle of 6.0°. Scans of (1.21 + 0.30 tanθ) were made at a speed of 8.0° min^{-1} (in omega). Weak reflections were rescanned and counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal-to-detector distance was 400.0 mm.

Of the 4293 reflections collected, 4022 were unique. The intensities of three representative reflections, measured after every 150 reflections, declined by −14.00%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient for Cu-Kα is 6.7 cm^{-1}. An empirical absorption correction, using the program DIFABS,[27] was applied which resulted in transmission factors ranging from 0.72 to 1.09. The data were corrected for Lorentz and polarisation effects.

The structure was solved by direct methods;[28] the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealised positions and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 1350 observed reflections [$I > 3.00\sigma(I)$] and 307 variable parameters and converged with agreement factors of R = 0.074 and R_w = 0.094.

Fig. 1 shows a PLUTO[29] drawing of the molecule. Lists of positional co-ordinates, bond lengths, bond angles and thermal parameters have been deposited with the C.C.D.C.*

1-*Benzyl*-4-tert-*butoxycarbonyl*-7-*methoxy*-1,3,4,4*a*-*tetrahydroindeno*[1,2-b]*pyrazin*-2-*one*, **9b**.—*Crystal data*. $C_{24}H_{26}N_2O_4$, M = 406.48, monoclinic, a = 28.928(3), b = 14.325(2), c = 11.580(1) Å; β = 112.671(6)°; U = 4428 Å^3, Z = 8, ρ_c = 1.219, μ(Cu-Kα) = 6.41 cm^{-1}, space group $C2/c$ (# 15), 2107 unique reflections with $I > 3\sigma(I)$, R = 6.6%.

A colourless tabular crystal, approximately 0.07 × 0.32 × 0.55 mm was mounted on a glass fibre for measurements. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 21 carefully-centred reflections in the range 66.23 < 2θ < 79.52° corresponded to a monoclinic cell. Data were collected at 22 ± 1 °C using the $\omega/2\theta$ scanning technique to a maximum 2θ value of 120.2°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.26° with a take-off angle of 6.0°. Scans of (1.10 + 0.30 tanθ) were made at a speed of 8.0° min^{-1} (in omega). Weak reflections were rescanned and counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 400.0 mm.

Of the 3527 reflections collected, 3449 were unique. The intensities of three representative reflections, measured after every 150 reflections, declined by −0.60%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient for Cu-Kα is 6.4 cm^{-1}. An empirical absorption correction, based on azimutal scans of several reflections, was applied which resulted in transmission factors ranging from 0.85 to 1.00. The data were corrected for Lorentz and polarisation effects.

The structure was solved by direct methods; the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealised positions and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 2107 observed reflections [$I > 3.00\sigma(I)$] and 271 variable parameters and converged with agreement factors of R = 0.066 and R_w = 0.090.

Fig. 2 shows a PLUTO drawing of the molecule. Lists of positional coordinates, bond lengths, bond angles and thermal parameters have been deposited with the C.C.D.C.*

1-*Benzyl*-4-tert-*butoxycarbonyl*-7-*methoxy*-1,3,4,9-*tetrahydroindeno*[1,2-b]*pyrazin*-2-*one* **11**.—*Crystal data*. $C_{24}H_{26}N_2O_4$, M = 406.48, triclinic, a = 12.29(1), b = 12.58(3), c = 7.144(5) Å; α = 96.1(1)°, β = 98.16(7)°, γ = 102.7(1)°; U = 1056 Å^3, Z = 2, ρ_c = 1.278, μ(Mo-Kα) = 0.82 cm^{-1}, space group $P\bar{1}$ (# 2), 3725 unique reflections with $I > 3\sigma(I)$, R = 4.1%.

A pink tabular crystal, approximately 0.08 × 0.24 × 0.26 mm was mounted on a glass fibre for measurements. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 23 carefully-centred reflections in the range 11.37 < 2θ < 19.57° corresponded to a triclinic cell. Data were collected at 23 ± 1 °C using the $\omega/2\theta$ scanning technique to a maximum 2θ value of 50°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.38° with a take-off angle of 6.0°. Scans of (1.21 + 0.30 tanθ) were made at a speed of 2.0° min^{-1} (in omega). Weak reflections were rescanned and counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of peak counting time to background counting time was 2:1. The diameter of the incident beam collimator was 0.5 mm and the crystal-to-detector distance was 258.0 mm.

Of the 3916 reflections collected, 3725 were unique. The intensities of three representative reflections, measured after every 150 reflections, declined by −1.10%. A linear correction factor was applied to the data to account for this phenomenon.

The linear absorption coefficient for Mo-Kα is 0.8 cm^{-1}. An empirical absorption correction, using the program DIFABS, was applied which resulted in transmission factors ranging from 0.83 to 1.15. The data were corrected for Lorentz and polarisation effects.

The structure was solved by direct methods; the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation in idealised positions and were assigned isotropic thermal parameters which were 20% greater than the equivalent B value of the atom to which they were bonded. The final cycle of full-matrix least-squares refinement was based on 1448 observed reflections

* For full details of the Cambridge Crystallographic Data Centre deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 1*, 1993, Issue 1.

[$I > 3.00\sigma(I)$] and 271 variable parameters and converged with agreement factors of $R = 0.041$ and $R_w = 0.048$.

Fig. 3 shows a PLUTO drawing of the molecule. Lists of positional coordinates, bond lengths, bond angles and thermal parameters have been deposited with the C.C.D.C.*

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