

UNPRODUCTIVE SIGMA AND PI COMPLEXES IN THE REACTION OF 2-CHLOROQUINOXALINE WITH PIPERIDINE IN DIMETHYL SULPHOXIDE

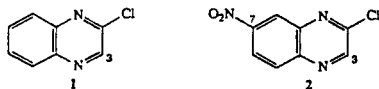
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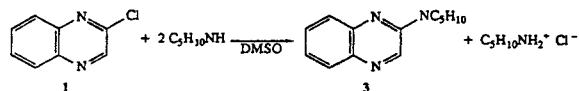
The rate of the reaction of 2-chloroquininoxaline with piperidine in dimethyl sulphoxide was measured over a wide range of amine concentrations and at several temperatures. It was found that the order with respect to the nucleophile is close to 1 between 300 and 320 K, but is definitely less at lower and higher temperatures. It is suggested that below 300 K an unreactive charge-transfer complex is formed between the reactants which dissociates at higher temperatures, whereas at temperatures higher than 320 K an unproductive σ complex is formed, the concentration of which increases with increase in temperature.

INTRODUCTION

The unorthodox behaviour of 2-chloro-7-nitroquininoxaline (**2**) towards piperidine has already been observed previously;¹ the results indicated that, contrary to intuition but in agreement with several data accumulated on similar systems,² the nucleophile first attacks the unsubstituted carbon atom at position 3 rather than the chlorine-bearing carbon atom 2.



We now report on the kinetic behaviour of 2-chloroquininoxaline (**1**) when reacted with piperidine (R_2NH) in dimethyl sulphoxide (DMSO) solvent.



RESULTS

The reaction was monitored spectrophotometrically at 379 nm, where only the product 2-piperidinoquinox-

aline absorbs. In several cases, the whole absorption spectrum of the medium was recorded, and showed a sharp isosbestic point near 348 nm.

The reactions were always strictly first order, as shown by applying the method of constant time intervals which gave excellent linear plots,³ with correlation coefficients at least 0.999. The method of constant time intervals is as follows: For a first order process leading from a reactant R to a product P, such as



the absorbance at any time A_t is given by

$$A_t = \epsilon_R [R] + \epsilon_P [P] = (\epsilon_R - \epsilon_P) [R]_0 e^{-kt} + \epsilon_P [R]_0$$

After a given time interval Δt , the absorbance is given by

$$A_{t+\Delta t} = \epsilon_R [R] + \epsilon_P [P] = (\epsilon_R - \epsilon_P) [R]_0 e^{-k(t+\Delta t)} + \epsilon_P [R]_0$$

and the absorbance variation ΔA is thus

$$\Delta A = (\epsilon_R - \epsilon_P) [R]_0 e^{-kt} (1 - e^{-k\Delta t})$$

If the absorbance A is recorded at constant time intervals Δt the $(1 - e^{-k\Delta t})$ term is constant during a run, and a plot of $\ln \Delta A$ vs t gives a straight line with slope $-k$. This method has the advantage that the rate constant k can be obtained without having to rely on the measurement of the absorbance at infinite time, which is often unreliable or has to be found by regression methods. The pseudo-monomolecular rate constants k_{obs} for a wide range of temperatures and piperidine concentrations are collected in Table 1.

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Table 1. Pseudo-monomolecular rate constants, k_{obs} , for the reaction of 2-chloroquinoline (QCl) with piperidine (R_2NH) in dimethyl sulphoxide

| $T = 293.4\text{ K},$ $C_{QCl} = 7.50 \times 10^{-5} \text{ mol l}^{-1}$ | | | $T = 298.4\text{ K},$ $C_{QCl} = 7.50 \times 10^{-5} \text{ mol l}^{-1}$ | | | $T = 303.4\text{ K},$ $C_{QCl} = 1.37 \times 10^{-4} \text{ mol l}^{-1}$ | | | $T = 308.4\text{ K},$ $C_{QCl} = 1.37 \times 10^{-4} \text{ mol l}^{-1}$ | | |
|---|--|--|---|--|--|---|--|--|---|--|--|
| $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | | $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | | $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | | $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | |
| 2.43 | 9.15×10^{-4} | | 2.43 | 4.35×10^{-3} | | 2.43 | 6.93×10^{-3} | | 2.43 | 1.00×10^{-5} | |
| 4.85 | 2.98×10^{-4} | | 4.85 | 1.02×10^{-3} | | 4.85 | 1.39×10^{-3} | | 4.85 | 1.50×10^{-5} | |
| 3.37 | 2.31×10^{-4} | | 3.37 | 5.86×10^{-4} | | 2.43 | 5.93×10^{-4} | | 2.43 | 6.22×10^{-4} | |
| 2.43 | 1.99×10^{-4} | | 2.43 | 5.05×10^{-4} | | 1.21 | 3.47×10^{-4} | | 1.21 | 3.81×10^{-4} | |
| 1.21 | 1.05×10^{-4} | | 1.21 | 2.22×10^{-4} | | 2.43 | 7.66×10^{-5} | | 2.43 | 2.03×10^{-4} | |
| 2.70 | 3.74×10^{-5} | | 6.74 | 1.53×10^{-4} | | 1.21 | 4.20×10^{-5} | | 4.18 | 1.42×10^{-4} | |
| 1.21 | 2.36×10^{-5} | | 2.43 | 4.20×10^{-5} | | 6.45 | 1.44×10^{-5} | | 4.05 | 1.32×10^{-4} | |
| 6.45 | 1.47×10^{-5} | | 1.21 | 2.80×10^{-5} | | 9.70 | 2.79×10^{-6} | | 2.67 | 8.00×10^{-5} | |
| 6.07 | 1.41×10^{-5} | | 6.45 | 1.23×10^{-5} | | | | | 2.08 | 7.20×10^{-5} | |
| 9.70 | 3.94×10^{-6} | | 9.70 | 1.10×10^{-5} | | | | | 1.35 | 4.17×10^{-5} | |
| | | | | 2.00×10^{-6} | | | | | 6.45 | 2.27×10^{-5} | |
| | | | | | | | | | 9.70 | 3.84×10^{-6} | |

| $T = 313.4\text{ K},$ $C_{QCl} = 1.37 \times 10^{-4} \text{ mol l}^{-1}$ | | | $T = 318.4\text{ K},$ $C_{QCl} = 9.89 \times 10^{-5} \text{ mol l}^{-1}$ | | | $T = 328.4\text{ K},$ $C_{QCl} = 9.89 \times 10^{-5} \text{ mol l}^{-1}$ | | | $T = 338.4\text{ K},$ $C_{QCl} = 9.89 \times 10^{-5} \text{ mol l}^{-1}$ | | |
|---|--|--|---|--|--|---|--|--|---|--|--|
| $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | | $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | | $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | | $[R_2NH]$ (mol l ⁻¹) | k_{obs} (s ⁻¹) | |
| 2.43 | 1.07×10^{-2} | | 2.43 | 8.23×10^{-3} | | 2.43 | 8.83×10^{-3} | | 2.43 | 9.67×10^{-3} | |
| 4.85 | 1.91×10^{-3} | | 4.85 | 1.97×10^{-3} | | 4.85 | 2.55×10^{-3} | | 4.85 | 3.00×10^{-3} | |
| 2.43 | 2.10×10^{-3} | | 1.21 | 6.13×10^{-4} | | 2.43 | 1.46×10^{-3} | | 2.43 | 1.73×10^{-3} | |
| 6.74 | 3.47×10^{-4} | | 4.05 | 2.00×10^{-4} | | 1.21 | 1.07×10^{-3} | | 1.21 | 1.11×10^{-3} | |
| 5.06 | 2.94×10^{-4} | | 2.02 | 1.35×10^{-5} | | 4.05 | 3.40×10^{-4} | | 4.05 | 5.41×10^{-4} | |
| 2.43 | 1.07×10^{-4} | | 1.35 | 7.55×10^{-5} | | 2.02 | 2.10×10^{-4} | | 2.02 | 2.95×10^{-4} | |
| 1.21 | 6.22×10^{-5} | | 6.45 | 4.28×10^{-5} | | 6.45 | 9.18×10^{-5} | | 6.45 | 1.35×10^{-4} | |
| 6.45 | 3.08×10^{-5} | | 9.70 | 7.98×10^{-6} | | 9.70 | 2.13×10^{-5} | | 9.70 | 3.45×10^{-5} | |
| 9.70 | 4.62×10^{-6} | | | | | | | | | | |

Table 2. Apparent order α (slope of the $\log k_{\text{obs}}/\log[R_2NH]$ straight lines) with respect to the piperidine concentration as a function of temperature

| $T(K)$ | 293.4 | 298.4 | 303.4 | 308.4 | 313.4 | 318.4 | 328.4 | 338.4 |
|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|
| α | 0.70 | 1.00 | 1.00 | 0.94 | 0.99 | 0.89 | 0.78 | 0.72 |
| s.d. ^a | 0.03 | 0.06 | 0.06 | 0.03 | 0.06 | 0.06 | 0.06 | 0.01 |

^a Three standard deviations as calculated by a non-linear least-squares fitting program.

Table 3. Fitting of the kinetic data to equation (6)

| <i>T</i> (K) | 293.4 | 298.4 | 303.4 | 308.4 | 313.4 | 318.4 | 328.4 | 338.4 |
|--|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|
| <i>k_{bi}</i> (l mol ⁻¹ s ⁻¹) | 8.07 × 10 ⁻⁴ | 2.03 × 10 ⁻³ | 2.76 × 10 ⁻³ | 2.76 × 10 ⁻³ | 4.18 × 10 ⁻³ | 4.38 × 10 ⁻³ | 6.40 × 10 ⁻³ | 7.67 × 10 ⁻³ |
| (<i>K_Π</i> + <i>K_Σ</i>)(kin) | 0.47 | (0.05) | (-0.01) | (0.06) | (-0.02) | 0.12 | 0.31 | 0.38 |
| (<i>K_Π</i> + <i>K_Σ</i>)(opt) | 0.53 | (0.01) | (0.01) | (0.01) | (0.01) | 0.15 | 0.34 | 0.42 |

The plots of log *k_{obs}* vs log [QCl] give the apparent 'orders' with respect to the concentration of piperidine. The results collected in Table 2 are, however, unexpected: the slopes deviate significantly from unity at several temperatures. The 'order' is close to 1.00 between 298 and 313 K, but definitely less outside this range.

This means that at both low and high temperatures, inhibition by high concentrations of piperidine is competing with the main reaction path. We suggest that a fast equilibrium is established between the quinoxaline and piperidine, leading to an unreactive intermediate, and that the low temperature complex is different from the high-temperature complex.

RATE EQUATION

For reasons which will be given below, let us call these two complexes Π and Σ respectively, and the corresponding equilibrium constants *K_Π* and *K_Σ*:

$$K_{\Pi} = \frac{[\Pi]}{[QCl][R_2NH]}; K_{\Sigma} = \frac{[\Sigma]}{[QCl][R_2NH]} \quad (1)$$

The concentrations of the two complexes are thus given by

$$[\Pi] = K_{\Pi}[QCl][R_2NH]; [\Sigma] = K_{\Sigma}[QCl][R_2NH] \quad (2)$$

Since the total amount of 2-chloroquinoxaline, *C_{QCl}*, at any time is the sum of the concentration of free 2-chloroquinoxaline [QCl] and that of the two complexes,

$$[QCl] + [\Pi] + [\Sigma] = C_{QCl} \quad (3)$$

the concentration of free 2-chloroquinoxaline [QCl] is given by

$$[QCl] = \frac{C_{QCl}}{1 + (K_{\Pi} + K_{\Sigma})[R_2NH]} \quad (4)$$

Assuming a rate equation of the form

$$v = k_{bi}[QCl][R_2NH] = k_{bi} \frac{C_{QCl}[R_2NH]}{1 + (K_{\Pi} + K_{\Sigma})[R_2NH]} \quad (5)$$

the expression for *k_{obs}* becomes

$$k_{obs} = \frac{v}{C_{QCl}} = k_{bi} \frac{[R_2NH]}{1 + (K_{\Pi} + K_{\Sigma})[R_2NH]} \quad (6)$$

The rate data in Table 2 were thus fitted, for every

temperature, to the equation

$$k_{obs} = \frac{x[RNH_2]}{1 + y[RNH_2]} \quad (7)$$

where *x* stands for *k_{bi}* and *y* for (*K_Π* + *K_Σ*). The resulting values for *x* and *y* are given in Table 3; the correlation coefficients were, in most cases, at least 0.9999. Values of (*K_Π* + *K_Σ*) less than 0.1 are too small to be of significance and will be considered as being zero.

An independent check of rate equation (6), was found by analysing the whole spectra recorded in several runs. A close examination of these spectra showed that the absorbances were sometimes lower than those calculated on the basis of the molar absorptivities of the constituents, and especially at high piperidine concentrations.

If we assume that neither Π nor Σ absorbs at 320 nm, the λ_{max} of QCl, the absorbance *A* (per cm) is given by

$$A = \epsilon_{QCl}[QCl] = \epsilon_{QCl} \frac{C_{QCl}}{1 + (K_{\Pi} + K_{\Sigma})[R_2NH]} \quad (8)$$

In the absence of complexation (i.e. *K_Π* + *K_Σ* = 0), the absorbance *A'* would be

$$A' = \epsilon_{QCl}C_{QCl} \quad (9)$$

Subtracting equation (8) from equation (9) gives the deviation Δ*A* from the expected absorbance:

$$\Delta A = A' - A = \epsilon_{QCl}C_{QCl} \frac{(K_{\Pi} + K_{\Sigma})[R_2NH]}{1 + (K_{\Pi} + K_{\Sigma})[R_2NH]} \quad (10)$$

which allows the calculation of the optical value of (*K_Π* + *K_Σ*):

$$(K_{\Pi} + K_{\Sigma})(opt) = \frac{1}{[R_2NH]} \frac{\Delta A}{\epsilon_{QCl}C_{QCl} - \Delta A} \quad (11)$$

The results are given in Table 3; the agreement between the (*K_Π* + *K_Σ*)(opt) and (*K_Π* + *K_Σ*)(kin) is quite satisfactory and lends considerable support to rate equation (6), and hence to the proposed mechanism.

The values of (*K_Π* + *K_Σ*), which are obtained indirectly, are, however, fairly inaccurate and cannot be used as such for further elaboration, such as in the evaluation of enthalpies.

MECHANISM

The value of (*K_Π* + *K_Σ*) is nearly zero between 298 and 313 K and rises at both ends of this range. Since the

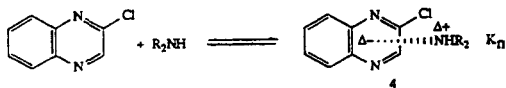
temperature dependence of an equilibrium constant K is related to the enthalpy ΔH^0 by

$$\frac{\partial K}{\partial T} = \frac{\Delta H^0}{RT^2} e^{-\Delta H^0/RT} \quad (12)$$

the sign of $\partial K/\partial T$ is that of ΔH^0 , i.e. K increases at higher temperatures when $\Delta H^0 > 0$ (endothermic) and increases at lower temperatures when $\Delta H^0 < 0$ (exothermic).

Since our K values go through a minimum, it means that there is a low temperature range where $\partial K/\partial T$ is negative, indicative of an exothermic association, the corresponding ($K_\Pi + K_\Sigma$) decreasing to nearly zero around 303 K. At 313 K the high-temperature range starts where $\partial K/\partial T$ is positive, and an endothermic association is to be considered.

The formation of π complexes between electron-deficient aromatic systems and electron-donor amines is probably an exothermic process. Hurst *et al.*³ have found that aromatic diazines form charge-transfer complexes with aromatic hydrocarbon donors and that, more specifically, C_6D_6 and pyrazine do associate with a ΔH of nearly zero (Enthalpies of formation for charge-transfer complexes are not frequently measured; for recent ΔH data for the I_2 -substituted complexes, see Ref. 4. The ΔH values for all these systems are negative. Many cases are known where σ -adduct formations are exothermic, but they all involve highly activated substrates such as 1,3,5-trinitrobenzene,⁵ 3,5-dinitropyridine⁶ or 2,4-dinitronaphthalene.⁷ Several other cases were presented by Terrier.⁸ In all cases reported, the electron-withdrawing groups cooperate to activate one or more positions; in quinoxaline, the 2- and 3-carbon atoms are activated by only one nuclear nitrogen atom. For such systems the formation of the complex occurs with excessively low equilibrium constants and the corresponding ΔH values are normally positive.) Since piperidine is a better donor than benzene and chloroquinoxaline a better acceptor than pyrazine, we expect a negative value for this ΔH . We therefore propose that the low temperature association corresponds to a Π complex such as 4.



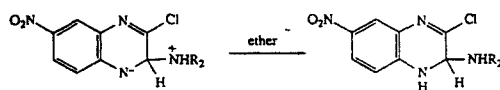
We cannot, of course, exclude the possibility that complex 4 corresponds to the full transfer of an electron, and would thus be a pair of radical-ions, similar to those observed by Grossi⁹ when π -deficient aromatics such as 2-chloroquinoline are reacted with tertiary amines in tetrahydrofuran, or by Bacaloglu *et al.*¹⁰ when hydroxide ions interact with dinitrobenzonitriles. It is clear, however, that our findings show that this intermediate is unproductive, and dissociates faster than it isomerizes to the Meisenheimer complex.

The addition of a nucleophile to an aromatic system, leading to an adduct similar to the Meisenheimer complex in nucleophilic aromatic substitution, is usually considered as an endothermic process since it is the major component of the overall activation energy; we therefore propose that the high-temperature association corresponds to the σ complex 5.



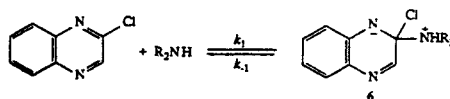
Such a preferred addition of a nucleophile to a position carrying no substituent has already been observed in several instances, and more specifically in the case of pyrazines¹¹ and quinoxalines.¹² Makosza *et al.*¹² have shown in a series of elegant experiments that 2-chloroquinoxaline is attacked faster at the unsubstituted 3-position than at the 2-position by nucleophiles such as α -chlorinated sulphone carbanions; in their case, however, the primary adduct undergoes further reactions leading to unexpected aziridine derivatives.

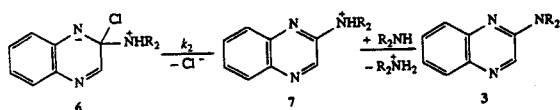
It was shown previously¹ that a similar adduct of piperidine to the 3-position of 2-chloro-7-nitroquinoxaline can undergo a proton transfer from the exocyclic ammonium nitrogen atom to the nuclear amide nitrogen atom when the reaction is run in diethyl ether, ultimately giving the doubly substituted product after air-induced oxidation. The difference between the two situations is probably to be ascribed to the poor stability of the zwitterion in diethyl ether and its good stabilization in dimethyl sulphoxide. It should be noticed that no disubstitution product was ever detected in the present work.



The major conclusion from our results is thus that for the present reaction, neither the π complex 4 nor the σ complex 5 is an intermediate in the substitution reaction, which means that their intramolecular isomerization to the σ complex 6 is a very slow process, unable to compete with the intermolecular dissociation-association mechanism.

If we now turn to the meaning of k_{bi} , we notice that this is the rate constant for the substitution reaction and we suggest, according to rate equation (7), that only the free quinoxaline undergoes the addition of piperidine in





a first reversible step, giving the short-lived σ complex **6**, which then spontaneously loses its halides ion Cl^- , the loss of the proton from intermediate **7** to give the product **3** being fast enough to be kinetically non-significant. The resulting expression for k_{bi} is thus

$$k_{bi} = \frac{k_1 k_2}{k_{-1} + k_2} \quad (13)$$

A plot of $\ln k_{bi}$ vs $1/T$ is shown in Figure 1; it is definitely non-linear, suggesting that k_{-1} and k_2 are of the same order of magnitude, and that there is a change in the rate-determining step on going from low to high temperatures. The data collected so far seem insufficient to make a suggestion regarding the rate-determining step at both temperature extremes.

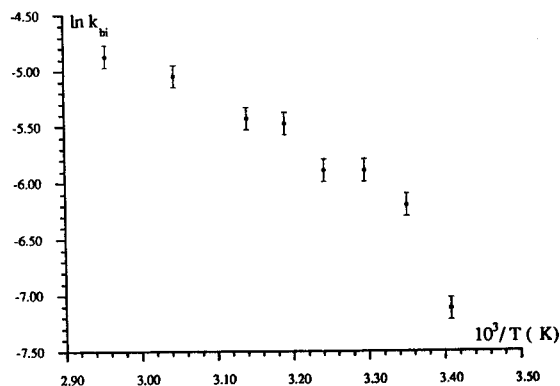


Figure 1. Plot of k_{bi} (from Table 3) as a function of $1/T$ (K)

EXPERIMENTAL

^1H NMR spectra were recorded in CDCl_3 on a Bruker VM250 spectrometer; chemical shifts are given in ppm downfield from internal TMS and J values are given in Hz. A Bruker IFS 25 spectrophotometer was used to measure the IR spectra. Mass spectra were obtained with a VG Micromass 70-70F instrument; peaks less than 10% of the base peak are omitted. HPLC was carried out on a Waters apparatus fitted with a UV (254 nm) detector, on $25 \text{ cm} \times 4.6 \text{ mm}$ i.d. columns packed with Rosil, $5 \mu\text{m}$; the flow rate was 2 ml min^{-1} . Most runs were analysed after completion, and showed over 95% conversion to piperidinoquinoxaline, together with small (2–5%) and highly variable amounts of quinoxalinone, the amount of which was independent of the concentration of piperidine. Melting

points, recorded on a Reichert hot-stage microscope, are uncorrected.

Piperidine and dimethyl sulphoxide were purified according to Perrin *et al.*¹³

The kinetics were followed with a Cary 2300 spectrometer in a thermostated compartment, and the faster runs were monitored with HP 8452 A diode-array spectrometer.

2-Chloroquinoxaline. *o*-Phenylenediamine was condensed with monochloroacetic acid according to Cuiban *et al.*¹⁴ to give 3,4-dihydro-2-hydroxyquinoxaline, which was oxidized with 30% alkaline hydrogen peroxide; recrystallization from propanol gave tan crystals of 2-hydroxyquinoxaline: m.p. $268\text{--}269^\circ\text{C}$, lit.¹⁴ $267\text{--}269^\circ\text{C}$; yield 96%, lit.¹⁴ 86%. 2-Hydroxyquinoxaline (5.00 g, 34.2 mmol) was refluxed for 3 h in 40 ml of freshly distilled phosphoryl chloride containing 10.4 g of pyrophorus pentachloride. Excess POCl_3 was then removed under reduced pressure, the residue poured into ice-water and the pH adjusted to 7. The product was then sublimed (10°C , 0.13 Pa) rather than recrystallized. 2-Chloroquinoxaline: m.p. 48°C , lit.¹⁵ $46\text{--}48^\circ\text{C}$; ^1H NMR ($\text{DMSO}-d_6$), δ 8.99 (1 H, d, H_3), 8.20 (1 H, dd, H_5) 8.10 (1 H, m, H_8), 7.9 (2 H, m, H_6 and H_7); $J_{3,6} = 0.3$, $J_{5,6} = 8.8$, $J_{5,7} = 1.5$; MS, m/z 164 (100%, M^+), 166 (35%), 129 (100, $\text{M}^+ - \text{Cl}^-$), 102 (47, $129 - \text{HCN}$, *).

2-Piperidinoquinoxaline. 2-Chloroquinoxaline (473 mg, 2.87 mmol) and piperidine (0.7 ml, 7.0 mmol) were kept in dry diethyl ether at room temperature; after work-up and recrystallization from light petroleum (b.p. $40\text{--}60^\circ\text{C}$), 477 mg (2.71 mmol) of pure substitution product were obtained as yellow needles. 2-Piperidinoquinoxaline: m.p. $62\text{--}63^\circ\text{C}$, lit.¹⁴ $62\text{--}63^\circ\text{C}$; yield 94%, lit.¹⁴ 100%; ^1H NMR (CDCl_3), δ 8.6 (1 H, d, H_3), 7.9 (1 H, dd, H_5), 7.7 (1 H, dd, H_8), 7.5 (1 H, ddd, H_6), 7.3 (1 H, dd, H_7), 3.8 (4 H, m, piperidine $\alpha\text{-CH}_2$), 1.7 (6 H, m, piperidine β - and $\gamma\text{-CH}_2$); $J_{3,6} = 0.3$, $J_{5,6} = J_{7,8} = 8.6$, $J_{5,7} = 1.4$, $J_{6,7} = 6.8$; MS, m/z 213 (15, M^+), 212 (100%, $\text{M}^+ - 1$), 211 (21), 184 (69, $\text{M}^+ - \text{C}_2\text{H}_5$), 169 (25), 157 (35, $184 - \text{HCN}$), 156 (26), 144 (17), 143 (14), 131 (14, $157 - 26$), 130 (50, $\text{M}^+ - \text{C}_5\text{H}_9\text{N}$), 129 (19, $156 - \text{HCN}$), 103 (11), 102 (19), 84 (22, $\text{C}_5\text{H}_{10}\text{N}^+$).

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