Chromone Studies. Part 4.[1] Structural Analysis of Chromone-derived 2-Amino-3-(2-hydroxybenzoyl)acrylamides

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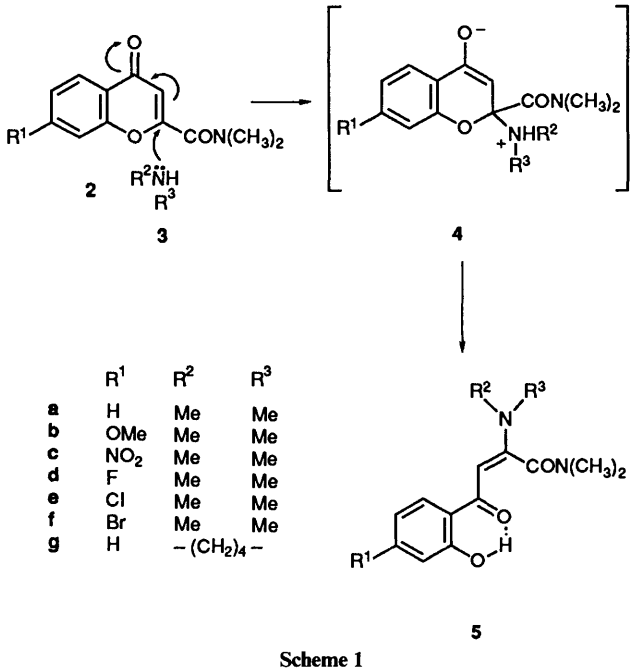
A combination of X-ray crystallographic, ^1H, ^{13}C NMR and IR spectroscopic, and computer-modelling techniques have been used to explore both configurational and conformational aspects of the structures of a series of substituted 2-amino-3-(2-hydroxybenzoyl)acrylamides.

Chromone derivatives such as disodium cromoglycate (DSCG **1**),[2] and certain chromone-2-carboxamides[3] are known to exhibit anti-allergic activity. In fact, DSCG **1** is widely used[4] in asthma therapy, its mode of action apparently involving, amongst other things, stabilisation of mast cells in the bronchial mucosa.[5,6] To our knowledge, however, the molecular basis for such action has yet to be established.[4-7] The susceptibility of chromones to ring opening, *via* C-2 attack by various nitrogen,[8] and oxygen nucleophiles,[9] has prompted us to explore the possible implication of this molecular process in chromone pharmacology. Thus, appropriate chromones may block or modify receptor interactions by binding covalently, through C-2, to biogenetic nucleophiles such as mast-cell proteins or inflammatory mediators like histamine[10] (Fig. 1). Consequently, we have begun a detailed examination of the reactions of chromone-2-carboxamides (**2**, Scheme 1) with amines as models for *in vivo* nucleophiles.



Scheme 1

In principle, ring opening of chromones may afford products having either *E*- or *Z*-double-bond configurations. Zagorevskii *et al.*,[11] in an earlier investigation of related systems, used ^1H NMR $J_{1,3}$ vinyl coupling constants and IR spectroscopy to establish: the *E*-configuration of *N,N*-disubstituted β-amino-vinylketones **6**; the *Z*-configuration of *N*-monosubstituted analogues **7**; and the significance of intra-molecular hydrogen bonding in both series. However, they were unable to determine the double-bond geometry in the products of reactions of 2-substituted chromones with secondary amines. In this communication we describe the use of X-ray crystallographic, spectroscopic and computer-modelling methods in elucidating the stereochemistry of such compounds **5**.

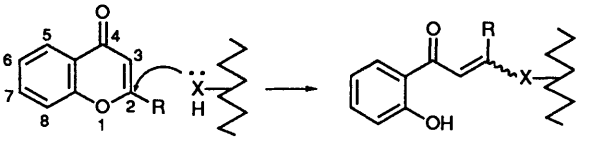
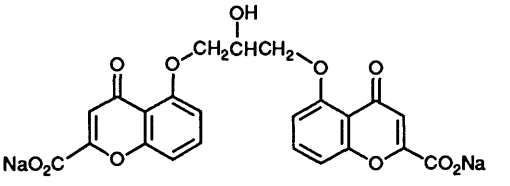
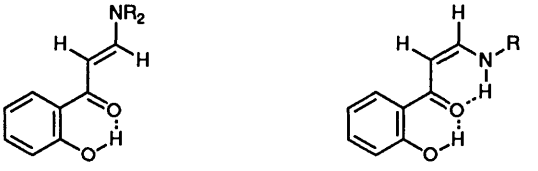


Fig. 1 Putative interaction of biogenetic nucleophiles (*e.g.* X = N, O, S) with chromone systems





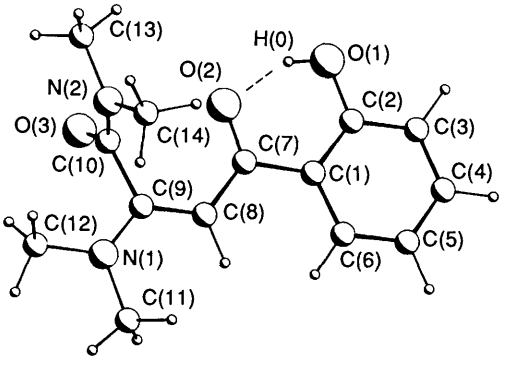


Fig. 2 X-Ray crystal structure of 2-(dimethylamino)-3-(2-hydroxybenzoyl)-*N,N*-dimethylacrylamide (**5a**), showing the crystallographic numbering

A definitive determination of the solid-state structure of the parent system **5a** was achieved by single crystal X-ray diffraction analysis. The crystal structure (Fig. 2) clearly indicates the *E*-geometry of the double bond in this compound. Other significant features of the solid state structure are: (i) intra-

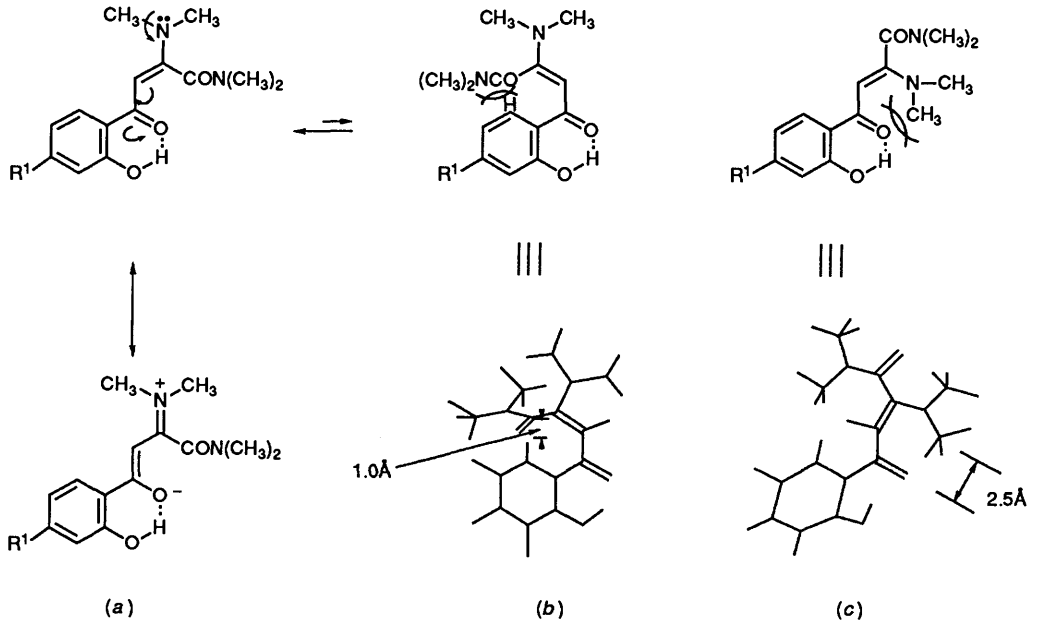


Fig. 3 (*a*) Favoured *E*-configuration of compounds **5a-f** illustrating delocalisation and hydrogen-bonded chelation. (*b*) Unfavourable steric interaction (see footnote * on p. 1183) in the alternative rotamer of the *E*-diastereoisomer. (*c*) Unfavourable steric interaction (see footnote * on p. 1183) in a planar conformation of the *Z*-diastereoisomer.

Table 1 Comparative ^1H and ^{13}C NMR chemical shifts for compounds **5a–f** (see Fig. 4)

^{13}C Nucleus	δ **5a**	$\Delta\delta^a$
CON*Me*$_2$	34.06	0.44
	36.84	0.46
NMe_2	39.38	0.52
	40.11	0.82
C-1	166.44	0.52
C-2	158.76	1.54
C-3	88.81	0.31
C-4	189.74	1.72
3-H[b]	5.75	0.12

[a] Maximum variation from value for compound **5a** in the series **5b–f**. [b] ^1H nucleus.

molecular hydrogen bonding between the phenolic hydroxy and the *syn*-orientated ketone carbonyl groups; (ii) the orthogonal (*ca.* 85°) arrangement of the planar* carboxamide moiety with respect to the rest of the molecule; and (iii) the remarkable co-planarity* of all of the remaining crystallographically determined atoms. The observed co-planarity is consistent with significant delocalisation of the dimethylamino nitrogen lone pair into the extended conjugated system, an effect which is, undoubtedly, enhanced by the hydrogen-bonding chelation (Fig. 3).

It is apparent, from IR and NMR spectroscopic data, that the solid-state (crystal) conformation of the parent system **5a** is essentially maintained in solution (in chloroform at least) and it may also be argued that the same configurational and conformational features, in fact, characterise all of the 2-amino-3-(2-hydroxybenzoyl)acrylamides **5a–g** examined. Thus the NMR data, obtained for $CDCl_3$ solutions, provide compelling evidence for *E*-geometry in each of the 2-amino-3-(2-hydroxybenzoyl)acrylamides **5a–g**. Firstly, the chemical shifts for the vinyl protons (3-H) and the non-aromatic carbons exhibit only marginal variations within the series (Table 1; Fig. 4), and the 3-

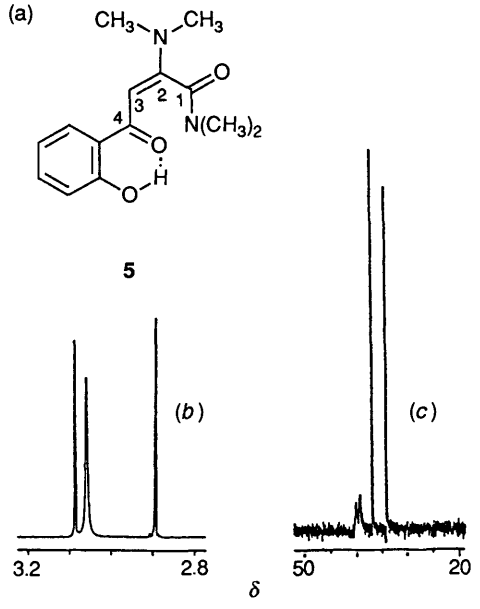


Fig. 4 (*a*) Compounds **5** with numbering (see Table 1 for NMR data); (*b*) partial ^1H NMR spectrum for **5d** (R^1 = F); (*c*) partial ^{13}C NMR spectrum for **5d** (R^1 = F)

H chemical shifts are closer to the calculated[12] value for the *E*-isomer (5.51 ppm) than for the *Z*-isomer (6.08 ppm). Secondly, in each of the compounds **5a–f**, both the amino- and carboxamido ^{13}C *N*-methyl signals are split [in the ^1H NMR spectra only the corresponding carboxamido signals are clearly split, the amino *N*-methyl signals typically appearing, at ambient temperature, as broad, post-coalescence singlets (Fig. 4)].† While slow site-exchange of *N*-alkyl groups is typical of *N*,*N*-disubstituted carboxamides, the parallel splitting of the dimethylamino ^{13}C signals is particularly significant, the implication being hindered rotation between resonance-stabilised

* Maximum deviations from the least-square planes were: 0.0820 Å (carboxamide moiety) and 0.0796 Å (rest of the molecule).

† The assignment of ^1H and ^{13}C NMR *N*-methyl signals is based on comparisons between the relevant spectra of the dimethylamino (**5a–f**) and pyrrolidino (**5g**) analogues.

planar conformers in which the *N*-methyl groups are diastereotopic. Such an arrangement is only possible if the acrylamides **5a–g** adopt the *E*-configuration illustrated in Fig. 3(*a*), since molecular modelling studies * clearly indicate that in the *Z*-diastereoisomer [Fig. 3(*c*)], co-planarity of the dimethylamino and vinyl ketone moieties is sterically prohibited. [Unfavourable steric interactions * would also destabilise the alternative planar rotamer, Fig. 3(*b*), even when the carboxamide moiety is perpendicular to the rest of the molecule.] The significance of these steric constraints is further illustrated by the orthogonal orientation of the carboxamide group in the crystal structure of the parent system **5a**. This orientation, which is presumably maintained in solution, obviates unfavourable steric interaction with the vinyl ketone oxygen without inhibiting lone-pair delocalisation in the independently planar carboxamide group.

IR carbonyl absorption band frequencies tend to be sensitive to structural change and it is noteworthy that, in the solid (KBr disc) and solution (chloroform) spectra of compounds **5a–g**, these bands exhibit minimal frequency variation (*ca.* ±10 cm^{-1}). Moreover, the general superposition of both ketone and carboxamide carbonyl absorption bands at low (*ca.* 1650 cm^{-1}) frequencies reflects effective delocalisation and concomitant reduction in the double-bond character of both carbonyl groups. Such frequency shifts are characteristic of planar carboxamide moieties but, more pertinently in this instance, argue independently for the essential co-planarity of the dimethylamino and aryl vinyl ketone systems. Furthermore, in both the solid state and solution IR spectra of each compound **5a–g**, the hydroxyl stretching band is shifted below 3000 cm^{-1}. This observation [together with the low field resonance (*ca.* δ 14) of the phenolic proton in the 60 MHz ^1H NMR spectrum of each compound] is indicative [11] of the strongly hydrogen-bonded chelate conformation illustrated in Fig. 3.

C-2 nucleophilic attack is, of course, equally likely at either face of the chromone-2-carboxamides (**2**, Scheme 1) and ring-opening (*via* racemic intermediates **4**) to the corresponding (*E*)-dimethylaminoacrylamides **5** may be attributed either to product development control or, in view of the reported [13] *E*/*Z*-configurational lability of related systems, to predominance of the more stable diastereoisomer. Effective π-participation by the dimethylamino nitrogen lone pair is expected to account for stabilisation of the essentially planar, conjugated *E*-products **5**, relative to the corresponding *Z*-isomers. In the mono-substituted amino analogues **7** examined by Zagorevskii *et al.*,[11] however, *syn*-orientated amino and vinyl ketone groups can achieve co-planarity without steric strain, and the configuration which permits 'double hydrogen bonding' is apparently favoured.

Experimental

^1H and ^{13}C NMR spectra were obtained from $CDCl_3$ solutions on Bruker AM 300 and WM 500 MHz or Varian Gemini 200 MHz spectrometers. Computer modelling was effected using Tripos Associates' software package, ALCHEMY II. The title compounds **5a–g** were obtained by treating the corresponding chromone-2-carboxamides **2a–f** [14] with ethanolic dimethylamine as illustrated in the following example (all coupling constant values *J* are given in Hz).

Dimethylamine (25% w/w solution in EtOH, 3.14 cm^3; 13.2 mmol) was added to a solution of *N*,*N*-dimethylchromone-2-carboxamide **2a** (0.500 g, 2.3 mmol) in dry EtOH (17 cm^3). After being stirred at room temperature (35 °C for the preparation of compounds **5b–g**) for 20 h, the solution was cooled and evaporated under reduced pressure to afford a crude solid (0.53 g) which was chromatographed † on silica (elution with EtOAc) to afford 2-(dimethylamino)-3-(2-hydroxybenzoyl)-*N*,*N*-dimethylacrylamide (**5a**) (0.374 g, 62%), m.p. 165–166 °C (from EtOH) (lit.,[15] 166–167 °C); δ_H(500 MHz; $CDCl_3$) 2.89 and 3.09 (6 H, 2 × s, $CONMe_2$), 3.06 (6 H, s, NMe_2), 5.75 (1 H, s, CH=C), 6.75–6.79 and 7.29–7.33 (2 H, 2 × m, 4′-H and 5′-H), 6.88 (1 H, dd, *J* 1 and 8, 3′-H), 7.67 (1 H, dd, *J* 2 and 8, 6′-H) and 13.60 (60 MHz; 1 H, s, OH); δ_C(75 MHz; $CDCl_3$) 34.06 and 36.84 ($CONMe_2$), 39.38 and 40.11 (NMe_2), 88.81 (C-3), 117.78 and 117.88 (C-3′ and C-5′), 120.18 (C-1′), 128.03 (C-6′), 133.75 (C-4′), 158.76 (C-2), 162.53 (C-2′), 166.44 (CO·N) and 189.74 (C-4); ν_{max}(KBr)/cm^{-1} 2920 and 1648.

Analytical data for new compounds are as follows. 2-(*Dimethylamino*)-3-(2-*hydroxy*-4-*methoxybenzoyl*)-N,N-*dimethylacrylamide* (**5b**) (0.212 g, 36%), m.p. 154–156 °C (from EtOAc); [*m*/*z* Found: 292.141 (M^+, 10%). $C_{15}H_{20}N_2O_4$ requires: 292.142]; δ_H(300 MHz; $CDCl_3$) 2.90 and 3.09 (6 H, 2 × s, $CONMe_2$), 3.04 (6 H, br s, NMe_2), 3.78 (3 H, s, OMe), 5.65 (1 H, s, CH=C), 6.31–6.37 (2 H, m, 3′-H and 5′-H), 7.58 (1 H, d, *J* 9, 6′-H) and 14.10 (60 MHz; 1 H, s, OH); δ_C(75 MHz; $CDCl_3$) 34.48 and 37.30 ($CONMe_2$), 39.47 and 40.09 (NMe_2), 55.37 (OCH_3), 89.12 (C-3), 101.02 and 106.43 (C-3′ and C-5′), 113.95 (C-1′), 129.63 (C-6′), 157.89 (C-2), 164.26 (C-4′), 165.33 (C-2′), 166.93 (CO·N) and 189.01 (C-4); ν_{max}(KBr)/cm^{-1} 2930, 1660 and 1650; *m*/*z* 292 (M^+, 10%) and 220 (100%).

2-(*Dimethylamino*)-3-(2-*hydroxy*-4-*nitrobenzoyl*)-N,N-*dimethylacrylamide* (**5c**) (0.305 g, 52%), m.p. 160–161 °C (from EtOAc) (Found: C, 54.8; H, 5.7; N, 13.5. $C_{14}H_{17}N_3O_5$ requires: C, 54.7; H, 5.6; N, 13.7%); δ_H(300 MHz; $CDCl_3$) 2.92 and 3.11 (6 H, 2 × s, $CONMe_2$), 3.07 and 3.19 (6 H, 2 × s, NMe_2), 5.71 (1 H, s, CH=C), 7.58 (1 H, dd, *J* 2 and 9, 5′-H), 7.69 (1 H, d, *J* 2, 3′-H) 7.79 (1 H, d, *J* 9, 6′-H) and 13.85 (60 MHz; 1 H, s, OH); δ_C(75 MHz; $CDCl_3$) 34.50 and 37.14 ($CONMe_2$), 39.90 and 40.93 (NMe_2), 89.04 (C-3), 112.28 and 113.52 (C-3′ and C-5′), 124.82 (C-1′), 128.87 (C-6′), 150.53 (C-4′), 160.30 (C-2), 163.09 (C-2′), 165.92 (CO·N) and 188.02 (C-4); ν_{max}(KBr)/cm^{-1} 2920 and 1645; *m*/*z* 307 (M^+, 11%) and 72 (100%).

2-(*Dimethylamino*)-3-(4-*fluoro*-2-*hydroxybenzoyl*)-N,N-*dimethylacrylamide* (**5d**) (0.228 g, 39%), m.p. 164–166 °C (from EtOAc) (Found: C, 59.7; H, 6.3; N, 10.0. $C_{14}H_{17}N_2O_3F$ requires: C, 60.0; H, 6.1; N, 10.0%); δ_H(300 MHz; $CDCl_3$) 2.89 and 3.08 (6 H, 2 × s, $CONMe_2$), 3.06 (6 H, br s, NMe_2), 5.63 (1 H, s, CH=C), 6.44–6.58 (2 H, m, 3′-H and 5′-H), 7.65 (1 H, dd, *J* 7 and 9, 6′-H) and 14.0 (60 MHz; 1 H, s, OH); δ_C(75 MHz; $CDCl_3$) 34.39 and 37.15 ($CONMe_2$), 39.59 and 40.40 (NMe_2), 88.96 (C-3), 104.73 and 105.81 (2 × d, $^2J_{CF}$ 23 and $^2J_{CF}$ 24, C-3′ and C-5′), 117.25 (d, $^4J_{CF}$ 3, C-1′), 130.18 (d, $^3J_{CF}$ 11, C-6′), 159.03 (C-2), 165.27 (d, $^3J_{CF}$ 15, C-2′), 166.10 (d, $^1J_{CF}$ 254, C-4′), 166.62 (CO·N) and 189.10 (C-4); ν_{max}(KBr)/cm^{-1} 2910 and 1660; *m*/*z* 280 (M^+, 9%) and 208 (100%).

3-(4-*Chloro*-2-*hydroxybenzoyl*)-2-(*dimethylamino*)-N,N-*dimethylacrylamide* **5e** (0.327 g, 55%), m.p. 124–125 °C (from EtOAc); [*m*/*z* Found: 296.092 (M^+, 12%). $C_{14}H_{17}N_2O_3Cl$ requires: 296.093]; δ_H(300 MHz; $CDCl_3$) 2.89 and 3.09 (6 H, 2 × s, $CONMe_2$), 3.07 (6 H, br s, NMe_3), 5.66 (1 H, s, CH=C), 6.74 (1 H, dd, *J* 2 and 9, 5′-H), 6.89 (1 H, d, *J* 2, 3′-H), 7.57 (1 H, d, *J* 9, 6′-H) and 13.85 (60 MHz; 1 H, s, OH); δ_C(75 MHz; $CDCl_3$) 34.48 and 37.07 ($CONMe_2$), 39.70 and 40.60 (NMe_2), 88.88 (C-3), 118.24 and 118.39 (C-3′ and C-5′), 118.85 (C-1′), 129.10 (C-6′), 139.32 (C-4′), 159.09 (C-2), 163.52 (C-2′), 166.45

* The required structures were modelled, and the resulting interatomic distances measured, using the software package, ALCHEMY II. The planar arrangements were obtained by altering the relevant torsion angles of energy-minimised structures.

† Preparative layer chromatography was typically employed to obtain analytical samples.

Table 2 Fractional coordinates ($\times 10^4$) for 2-(dimethylamino)-3-(2-hydroxybenzoyl)-*N*,*N*-dimethylacrylamide[a,b]

Atom	*x*/*a*	*y*/*b*	*z*/*c*
C(1)	3 746(3)	2 544(2)	7 544(2)
C(2)	4 446(3)	1 354(2)	8 181(2)
C(3)	3 164(4)	227(3)	8 319(3)
C(4)	1 200(4)	271(3)	7 832(3)
C(5)	472(4)	1 427(3)	7 209(3)
C(6)	1 730(3)	2 549(3)	7 066(3)
O(1)	6 362(3)	1 258(2)	8 686(2)
H(0)	6 934(51)	2 084(37)	8 613(32)
O(2)	6 909(2)	3 670(2)	7 972(2)
C(7)	5 145(3)	3 749(2)	7 440(2)
C(8)	4 480(3)	4 935(2)	6 764(2)
C(9)	5 709(3)	6 084(2)	6 666(2)
C(10)	7 921(3)	6 067(2)	7 141(2)
N(1)	5 105(3)	7 253(2)	6 094(2)
C(11)	3 046(4)	7 375(3)	5 518(3)
C(12)	6 442(4)	8 452(3)	5 964(3)
O(3)	8 996(2)	5 627(2)	6 412(2)
N(2)	8 558(3)	6 626(2)	8 313(2)
C(13)	10 644(4)	6 488(3)	8 826(3)
C(14)	7 234(5)	7 056(4)	9 187(3)

[a] For atom labelling, see Fig. 2. [b] Estimated standard deviations in parentheses.

Table 3 Selected bond lengths/Å and angles/° for 2-(dimethylamino)-3-(2-hydroxybenzoyl)-*N*,*N*-dimethylacrylamide[a,b]

C(1)–C(7)	1.489(3)	C(2)–O(1)	1.351(3)
O(1)–H(0)	0.87(3)	O(2)–C(7)	1.263(2)
C(7)–C(8)	1.422(3)	C(8)–C(9)	1.374(3)
C(9)–C(10)	1.526(3)	C(9)–N(1)	1.340(3)
C(10)–O(3)	1.222(3)	C(10)–N(2)	1.339(3)
N(1)–C(11)	1.464(3)	N(1)–C(12)	1.465(3)
N(2)–C(13)	1.465(3)	N(2)–C(14)	1.458(3)
C(2)–C(1)–C(7)	119.3(2)	C(6)–C(1)–C(7)	123.0(2)
C(1)–C(2)–O(1)	122.1(2)	C(3)–C(2)–O(1)	117.3(2)
C(2)–O(1)–H(0)	106.0(2)	C(1)–C(7)–O(2)	117.6(2)
C(1)–C(7)–C(8)	120.1(2)	O(2)–C(7)–C(8)	122.3(2)
C(7)–C(8)–C(9)	122.1(2)	C(8)–C(9)–C(10)	121.3(2)
C(8)–C(9)–N(1)	123.6(2)	C(10)–C(9)–N(1)	115.0(2)
C(9)–C(10)–O(3)	118.2(2)	C(9)–C(10)–N(2)	117.1(2)
O(3)–C(10)–N(2)	124.5(2)	C(9)–N(1)–C(11)	121.1(2)
C(9)–N(1)–C(12)	123.0(2)	C(11)–N(1)–C(12)	115.9(2)
C(10)–N(2)–C(13)	117.8(2)	C(10)–N(2)–C(14)	123.1(2)
C(13)–N(2)–C(14)	117.5(2)		

[a] For atom labelling, see Fig. 2. [b] Estimated standard deviations in parentheses.

(CO·N) and 188.99 (C-4); ν_{max}(KBr)/cm^{-1} 2920 and 1660; *m*/*z* 296 (^{35}Cl, M$^+$, 12%) and 224 (100%).

3-(4-*Bromo*-2-*hydroxybenzoyl*)-2-(*dimethylamino*)-N,N-*dimethylacrylamide* (**5f**) (0.265 g, 46%), m.p. 124–125 °C (from EtOAc) (Found: C, 49.2; H, 5.1; N, 8.4. $C_{14}H_{17}N_2O_3Br$ requires: C, 49.3; H, 5.0; N, 8.2%); δ_H(300 MHz; $CDCl_3$) 2.89 and 3.08 (6 H, 2 × s, $CONMe_2$), 3.06 (6 H, 2 × s, NMe_2), 5.65 (1 H, s, CH=C), 6.89 (1 H, dd, *J* 2 and 9, 5′-H), 7.06 (1 H, d, *J* 2, 3′-H), 7.50 (1 H, d, *J* 9, 6′-H) and 13.80 (60 MHz; 1 H, s, OH); δ_C(75 MHz; $CDCl_3$) 34.40 and 37.11 ($CONMe_2$), 39.74 and 40.52 (NMe_2), 88.88 (C-3), 119.30 (C-1′), 121.28 and 121.40 (C-3′ and C-5′), 127.63 (C-4′), 129.21 (C-6′), 159.33 (C-2), 163.56 (C-2′), 166.49 (CO·N) and 189.28 (C-4); ν_{max}(KBr)/cm^{-1} 2920 and 1660; *m*/*z* 340 (^{79}Br, M$^+$, 6%) and 72 (100%).

3-(2-*Hydroxybenzoyl*)-N,N-*dimethyl*-2-*pyrrolidinoacrylamide* (**5g**) (0.594 g, 90%), m.p. 183–184 °C (from EtOH) (Found: C, 66.3; H, 7.05; N, 9.2. $C_{16}H_{20}N_2O_3$ requires: C, 66.65; H, 7.0; N, 9.7); δ_H(200 MHz; $CDCl_3$) 1.86–2.11 [4 H, m, $CH_2(CH_2)_2CH_2$], 2.94 and 3.11 (6 H, 2 × s, $CONMe_2$), 3.36–3.45 and 3.65–3.72 [3 H and 1 H, 2 × m, $N(CH_2)_2$], 5.72 (1 H, s, CH=C), 6.76–6.93 (2 H, m, 4′-H and 5′-H), 7.28–7.37 (1 H, m, 3′-H), 7.69 (1 H, dd, *J* 2 and 8, 6′-H) and 13.70 (60 MHz; 1 H, s, OH); δ_C(50 MHz; $CDCl_3$) 24.82 and 25.39 [$CH_2(CH_2)_2CH_2$], 34.41 and 37.24 (2 × NMe), 48.57 and 48.78 [$N(CH_2)_2$], 89.84 (C-3), 118.30 and 118.61 (C-3′ and C-5′), 120.70 (C-1′), 128.62 (C-6′), 134.35 (C-4′), 156.74 (C-2), 163.31 (C-2′), 167.65 (CO·N) and 190.44 (C-4); ν_{max}(KBr)/cm^{-1} 2930, 2870 and 1650; *m*/*z* 288 (M$^+$, 2%) and 121 (100%).

Crystal Data.—$C_{14}H_{18}N_2O_3$, *M* = 262.31. Triclinic, *a* = 6.8745(6), *b* = 9.353(1), *c* = 10.872(1) Å, α = 94.536(8), β = 99.245(8), γ = 91.223(8)°, *V* = 687.4(1) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, λ = 0.7093 Å), space group $P\bar{1}$, *Z* = 2, D_x = 1.264 g cm^{-3}, yellow blocks, μ = 0.71 cm^{-1}.

Data Collection and Processing.—CAD4 diffractometer, ω–2θ mode with ω scan width = 0.5 + 0.35 tan θ, variable ω scan speed (max = 5.49° min^{-1}), graphite-monochromated Mo-Kα radiation: 4195 reflections measured ($2 \leq \theta \leq 30°$, *h*:$\bar{9}$–9, *k*:$\bar{13}$–13, *l*:0–15), 3260 observed with $I > \sigma(I)$. No crystal decay observed.

Structure Analysis and Refinement.—Direct methods[16] followed by full-matrix least-squares refinement with all non-hydrogen atoms anisotropic, and hydrogen atoms (with the exception of the phenolic hydrogen) in calculated positions with common isotropic temperature factors. The phenolic hydrogen [H(0)] was located from a difference Fourier map and its position refined. H(0) is involved in an intramolecular hydrogen bond: O(1)–H(0) 0.87(3) Å; O(2)···H(0) 1.69(3) Å; and O(1)–H(0)···O(2) 150.0(2)°. Unit weights were used. The final *R* value was 0.069 (190 parameters). Final fractional atomic coordinates are given in Table 2, and some selected bond lengths and angles are presented in Table 3. A diagram of the molecule appears in Fig. 2. Full lists of bond lengths and bond angles, thermal parameters and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre (CCDC).*

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* For details, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 2*, 1991, Issue 1.

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