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6-(2-Hydroxybenzoyl)-5-(pyrrol-2-yl)-3*H*-pyrrolizine

Sankar Prasad Dey,[a] Dilip Kumar Dey,[b] Asok Kumar Mallik[c] and Lutz Dahlenburg[d]*

[a]Department of Chemistry, Srikrishna College, Bagalu 741 502, Nadia, West Bengal, India, [b]Department of Chemistry, Chandidas Mahavidyalaya, Khujutipara 731 215, Birbhum, West Bengal, India, [c]Department of Chemistry, Jadavpur University, Kolkata 700 032, West Bengal, India, and [d]Institut für Anorganische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen, Germany
Correspondence e-mail: dahlenburg@chemie.uni-erlangen.de

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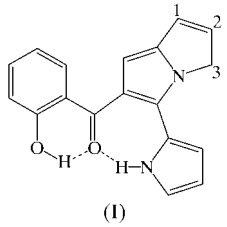
The title compound, 2-hydroxyphenyl 5-(pyrrol-2-yl)-3*H*-pyrrolizin-6-yl ketone, $C_{18}H_{14}N_2O_2$, was isolated from the base-catalyzed 1:2 condensation of 2-hydroxyacetophenone with pyrrole-2-carbaldehyde. The pyrrole N—H and hydroxybenzoyl O—H groups are hydrogen bonded to the benzoyl O atom. The allylic C=C double bond of the 3*H*-pyrrolizine system is located between ring positions 1 and 2, the C atom at position 3 (adjacent to the N atom) being single bonded.

Comment

The base-catalyzed Claisen–Schmidt reaction between equimolar quantities of 2-hydroxyacetophenone and benzaldehyde is among the most common synthetic routes to 2-hydroxychalcone, a compound that is useful in the synthesis of flavonoid compounds (Geissman, 1962; Harborne *et al.*, 1975; Mallik *et al.*, 1989, 1992). It has also been found that base-catalyzed 1:2 condensations between 2-hydroxyacetophenones and *p*-nitrobenzaldehyde in aqueous methanol gave *trans*-2,3-dimethoxy-3-(*p*-formylphenylamino)-4′-nitroflavanones as interesting novel products (Mallik *et al.*, 1992).



(I)

This encouraged us to study similar 1:2 condensations between phenyl methyl ketones and pyrrole-2-carbaldehyde, from which we obtained mixtures containing the usual (*E*)-1-acyl-3-(pyrrol-2-yl)-2-propen-1-ones but also 6-acyl-5-(pyrrol-2-yl)-3*H*-pyrrolizines as unexpected novel products (Mallik *et al.*, 2002). Pyrrolizines and their derivatives are of considerable interest in view of both their occurrence as natural products and their potential biological activities.

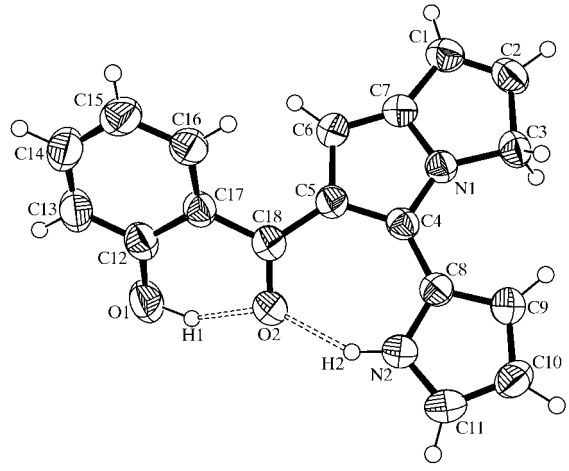


Figure 1
View of (I), with ellipsoids at the 50% probability level. The intramolecular hydrogen bonds are shown as double dashed lines.

Although the basic structural features of the new compounds could be established by detailed NMR studies (Mallik *et al.*, 2002), there remained some ambiguity with respect to the exact position of the allylic C=C double bond in the 3*H*-pyrrolizine system, for which there exist two conceivable alternatives, *viz*. either between ring positions 1 and 2 (see *Scheme*) or between the C atoms located at sites 2 and 3 (Jones, 1984). The X-ray structure analysis carried out for the 1:2 condensation product (I), formed from 2-hydroxyacetophenone and pyrrole-2-carbaldehyde, showed the allylic C=C bond to be located between atoms C1 and C2 [1.327 (3) Å], atoms C2 and C3 of the 3*H*-pyrrolizine system being connected by a single bond [1.493 (3) Å]. The interatomic distances within the C—N—C units of the unsaturated bipyrrolyl part of the 5-(pyrrol-2-yl)-3*H*-pyrrolizine moiety, *viz*. C4—N1—C7 and C8—N2—C11, span the relatively small range 1.351 (3)–1.380 (2) Å, which is about 0.14 Å longer than calculated for a C=N double bond but ∼0.10 Å shorter than the value of 1.459 (2) Å determined for the C—N single bond between C3 and N1. The substantial degree of π-electron delocalization evidenced from these bond lengths is also mirrored by the C—C distances within the two unsaturated five-membered rings, which are 1.422 (3), 1.432 (3) and 1.357 (3) Å for the C4—C5—C6—C7 chain and 1.381 (3), 1.397 (3) and 1.360 (3) Å for the C8—C9—C10—C11 chain (Table 1).

The formation of two intramolecular hydrogen bonds, O1—H1···O2 and N2—H2···O2 (Fig. 1 and Table 2), results in a slightly skewed overall geometry for (I), which is best described by the torsion angles given in Table 1 or by the angles between the least-squares planes through the 3*H*-pyrrolizine system (1), the pyrrole ring (2), and the *o*-hydroxybenzoyl building block (3) of 1–2 = 5.42 (11)°, 1–3 = 46.15 (5)° and 2–3 = 46.52 (7)°.

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Experimental

20% aqueous ethanolic KOH (10 ml) was added dropwise to a mixture of 2-hydroxyacetophenone (1 mmol) and pyrrole-2-carbaldehyde (2 mmol) in ethanol (10 ml). After 4 d under ambient conditions, the mixture was diluted with water (20 ml), carefully acidified by dropwise addition of 1 *M* HCl at 278 K, and subsequently extracted with chloroform. Concentration of the chloroform extract followed by chromatography over silica gel allowed the red condensation product, (I), to be separated from orange (*E*)-1-(2-hydroxyphenyl)-3-(pyrrol-2-yl)-2-propen-1-one, which resulted from a normal 1:1 Claisen–Schmidt condensation reaction (Mallik *et al.*, 2002). Single crystals were grown by slow evaporation of a chloroform–petroleum ether solvent mixture.

Crystal data

$C_{18}H_{14}N_2O_2$
M_r = 290.31
Monoclinic, $P2_1/c$
a = 8.6868 (7) Å
b = 22.0328 (13) Å
c = 7.592 (3) Å
β = 104.407 (16)°
V = 1407.4 (6) Å^3
Z = 4
D_x = 1.37 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 8.4–12.7°
μ = 0.09 mm^{-1}
T = 293 (2) K
Block, red
0.40 × 0.15 × 0.15 mm

Data collection

Nonius MACH3 diffractometer
Non-profiled ω scans
2666 measured reflections
2499 independent reflections
1796 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.2°
$h = -10 \rightarrow 0$
$k = -26 \rightarrow 0$
$l = -8 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Table 1
Selected geometric parameters (Å, °).

O1—C12	1.358 (3)	C4—C5	1.422 (3)
O2—C18	1.258 (2)	C4—C8	1.445 (3)
N1—C4	1.356 (2)	C5—C6	1.432 (3)
N1—C7	1.380 (2)	C5—C18	1.446 (3)
N1—C3	1.459 (2)	C6—C7	1.357 (3)
N2—C11	1.351 (3)	C8—C9	1.381 (3)
N2—C8	1.373 (2)	C9—C10	1.397 (3)
C1—C2	1.327 (3)	C10—C11	1.360 (3)
C1—C7	1.445 (3)	C17—C18	1.481 (3)
C2—C3	1.493 (3)		
C4—N1—C7	111.59 (15)	C7—C6—C5	107.30 (17)
C4—N1—C3	137.01 (16)	C6—C7—N1	108.12 (16)
C7—N1—C3	111.40 (15)	C6—C7—C1	144.8 (2)
C11—N2—C8	110.24 (18)	N1—C7—C1	107.09 (17)
C2—C1—C7	108.72 (19)	N2—C8—C9	106.17 (17)
C1—C2—C3	111.82 (18)	N2—C8—C4	123.06 (17)
N1—C3—C2	100.95 (16)	C9—C8—C4	130.74 (18)
N1—C4—C5	105.56 (16)	C8—C9—C10	107.96 (18)
N1—C4—C8	120.28 (16)	C11—C10—C9	107.59 (19)
C5—C4—C8	134.09 (17)	N2—C11—C10	108.04 (19)
C4—C5—C6	107.42 (16)	O2—C18—C5	121.90 (18)
C4—C5—C18	128.38 (17)	O2—C18—C17	117.63 (17)
C6—C5—C18	124.08 (17)	C5—C18—C17	120.43 (17)
N1—C4—C8—N2	−178.23 (17)	C4—C5—C18—C17	162.63 (19)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.98 (3)	1.68 (3)	2.584 (2)	151 (2)
N2—H2···O2	0.91 (2)	1.87 (2)	2.699 (2)	150 (2)

Refinement

Refinement on F^2
$R(F)$ = 0.043
$wR(F^2)$ = 0.113
S = 1.03
2499 reflections
208 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0518P)^2 + 0.2924P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.15 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0134 (19)

With the exception of the hydroxy O—H and pyrrole N—H atoms H1 and H2, which were allowed to refine freely, all H atoms were refined in geometrically idealized positions employing a riding model with isotropic displacement parameters constrained to 1.2 times U_{eq} of their respective carrier atoms.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1012). Services for accessing these data are described at the back of the journal.

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