

11-Methyl-2,3-benzodipyrin-1-one

Raymond Bonnett,^{a*} Majid Motevalli,^a Fiona J. Swanson^a
and María Asunción Vallés^b^aDepartment of Chemistry, Queen Mary, University of London, Mile End Road, London E1 4NS, England, and ^bDepartament de Química Orgànica, Facultat de Química, Universitat de Barcelona, Martí i Franquès 1-11, Barcelona 08028, Spain
Correspondence e-mail: r.bonnett@qmul.ac.uk

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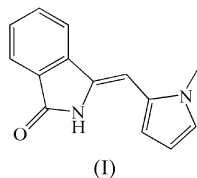
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The title compound {alternative names: 11-methyl-2,3-benzopyrromethenone and 3-[(1-methylpyrrol-2-yl)methylidene]-2,3-dihydro-1*H*-isoindol-1-one}, C₁₄H₁₂N₂O, was prepared by the base-catalysed condensation of phthalimidine with 2-formyl-1-methylpyrrole; yellow orthorhombic crystals, space group *Pbca*, were obtained from ethanol. The molecule is almost planar, having *Z*(−)antiperiplanar geometry. The molecules are arranged in pairs with intermolecular hydrogen bonding between lactam functions. Comparison with literature values for polyalkyldipyrin-1-ones shows that, apart from the local constraints of the benzene ring, the fused benzo ring has little effect on the molecular dimensions of the dipyrin-1-one skeleton.

Comment

Bilirubin, which adopts a ridge-tile structure with extensive intramolecular hydrogen bonding in the crystal (Bonnett *et al.*, 1978), contains two inequivalent dipyrin-1-one (pyrromethenone) units. Such units also occur in a variety of other plant and animal linear tetrapyrroles. Hence, the crystal structures of dipyrin-1-ones have attracted some attention [for a review, see Sheldrick (1983)]. We have also had an interest in dipyrin-1-ones as potential building blocks for the synthesis of benzoporphyrins (Bonnett & McManus, 1996; Valles *et al.*, 1996).



This report concerns the 2,3-benzodipyrin-1-one system, as the 11-methyl derivative, (I). Few representatives of this system have been described (Swanson, 1991; Boiadjev & Lightner, 2003*a*), and we have found no previous X-ray crystal

structure determination in this series. However, X-ray analyses have been reported for two distantly related structures, namely 3-[(pyrrol-2-yl)methylidene]indolin-2-one, derived from 2-oxindole (Boiadjev & Lightner, 2003*b*), and 3-benzylideneisoindolin-1-one (Mukherjee *et al.*, 2000). The photophysical properties of (I) in organic solvents and in micellar preparations have been reported (Gerhardt *et al.*, 2003), but the compound was there formulated with the *Z*-*syn* geometry.

The molecular structure of (I) is shown in Fig. 1. X-Ray analysis shows that the molecule has a 4-*Z*-antiperiplanar geometry, the chromophore being essentially planar, with N10–C4–C5–C6 and C4–C5–C6–N11 torsion angles of –2.0 (3) and 178.05 (16)°, respectively. Cullen *et al.* (1979) reported a similar geometry for 11-methyl-2,3-dimethyldipyrin-1-one and, as with that compound, the molecules

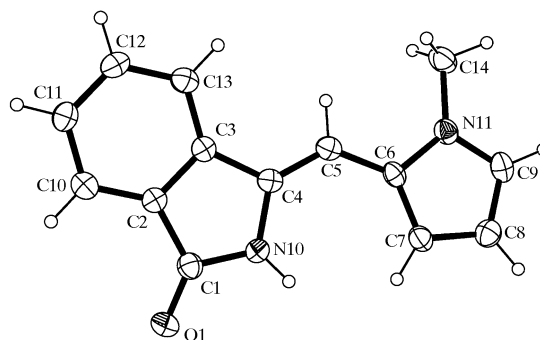


Figure 1

The molecular structure of (I). Ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

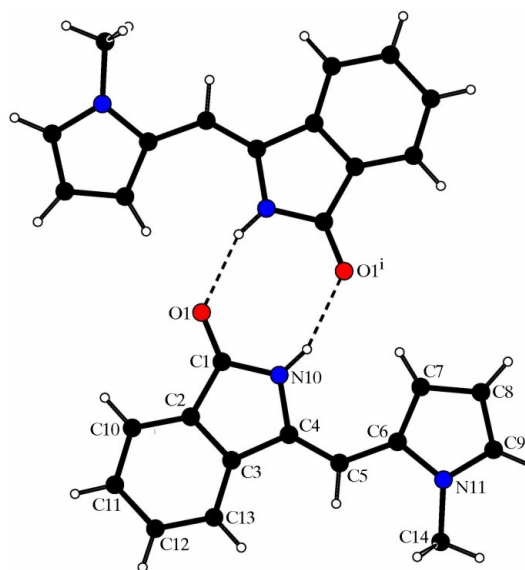
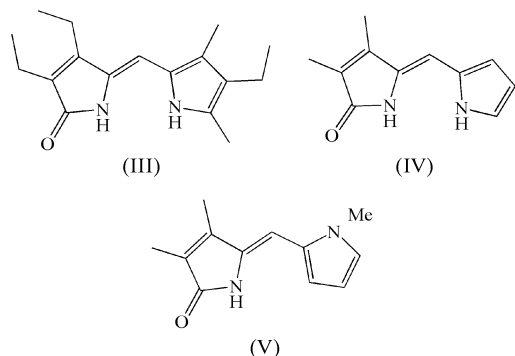


Figure 2

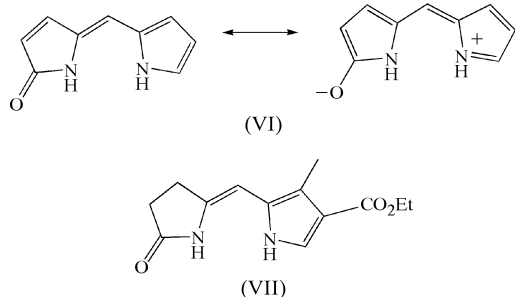
The dimeric assembly of (I), involving hydrogen-bonded (dashed lines) lactam groups. [Symmetry code: (i) $-x + 1, -y, -z$.]

in (I) are arranged in the crystal as dimers, with intermolecular hydrogen bonding between lactam groups (Table 1 and Fig. 2).



The bond lengths and angles observed here are similar to those observed in other 4-*Z*-dipyrrin-1-ones, namely (III) (Cullen *et al.*, 1977), (IV) and (V) (Cullen *et al.*, 1979), all of which have only alkyl substitution. The main difference, as might be anticipated, is in the region of the benzenoid ring; thus, the C2–C3 bond length in (I), at 1.391 (2) Å, is significantly longer than the average (1.325 Å) of that bond length for compounds (III)–(V). It may be noted that 4-*E*-dipyrrin-1-ones have also been prepared, typically by photoisomerization of the *Z* compounds, and X-ray structures are available (Sheldrick *et al.*, 1977; Hori *et al.*, 1981).

Other comparisons are made in Table 2. The bond lengths around the C5 bridge are of interest. The C4–C5 bond is slightly longer than expected for a double bond [although this discrepancy is marginal for (I), it still occurs], and the C5–C6 bond is slightly shorter than expected for a single bond. These changes are in accord with the pattern of delocalization shown in (VI). Cullen *et al.* (1979) have noted that the C1–N10 bond is significantly shorter than the C4–N10 bond, and this is also apparent in the 2,3-benzo derivative (I). We attribute this fact to the well known partial double-bond character of the C–N bond in amide functions. There is also a difference in length between the C9–N11 and C6–N11 bonds, the former being the shorter because of the delocalization represented in (VI). Although this delocalization can occur in (I) (although it is less pronounced because of the formal disruption of the benzenoid ring), it cannot occur in the *Z*-2,3-dihydro system (VII), and in this example the C9–N11 bond [1.386 (5) Å] is actually increased with respect to the C6–N11 bond



[1.373 (5) Å] (Gossauer *et al.*, 1976) because of delocalization to the 9-ethoxycarbonyl group.

Experimental

Compound (I) was prepared as follows (Swanson, 1991). A solution of phthalimidine (isoindol-1-one, 0.63 g) and 2-formyl-1-methylpyrrole (0.51 g) in ethanol (25 ml) was treated with aqueous sodium hydroxide (4 *M*, 20 ml) and heated under reflux for 7 h. The resulting yellow–orange solution was poured into ice-water. The bright-yellow precipitate was filtered off and washed with water to give a bright-yellow powder (0.30 g). Extraction of the filtrate with chloroform gave a further 0.05 g. The combined yellow solids were crystallized from ethanol to give (I) (0.19 g, 20%) as fine yellow needles (m.p. 471–475 K, with decomposition). Working on a larger scale allowed the yield to be increased to 40%. λ_{\max} (MeOH): 386 nm (ϵ 21 200 M⁻¹ cm⁻¹). ν_{\max} (KBr): 3400–3200, 1680, 1610, 1470, 1430, 1320 cm⁻¹. Analysis calculated for C₁₄H₁₂N₂O: C 75.00, H 5.36, N 12.50%; found: C 74.83, H 5.32, N 12.45%. Single crystals suitable for X-ray analysis were grown from ethanol.

Crystal data

C ₁₄ H ₁₂ N ₂ O	Mo <i>K</i> α radiation
<i>M_r</i> = 224.26	Cell parameters from 2787 reflections
Orthorhombic, <i>Pbca</i>	θ = 2.9–27.5°
<i>a</i> = 19.5886 (14) Å	μ = 0.08 mm ⁻¹
<i>b</i> = 13.8924 (9) Å	<i>T</i> = 120 (2) K
<i>c</i> = 8.3714 (3) Å	Slab, yellow
<i>V</i> = 2278.1 (2) Å ³	0.26 × 0.14 × 0.05 mm
<i>Z</i> = 8	
<i>D_x</i> = 1.308 Mg m ⁻³	

Data collection

Bruker–Nonius FR591 rotating-anode diffractometer	1530 reflections with <i>I</i> > 2σ(<i>I</i>)
φ and ω scans	<i>R</i> _{int} = 0.074
Absorption correction: multi-scan (<i>SADABS</i> ; Sheldrick, 2003)	θ_{\max} = 27.5°
<i>T</i> _{min} = 0.978, <i>T</i> _{max} = 0.996	<i>h</i> = -18 → 25
11 508 measured reflections	<i>k</i> = -14 → 18
2597 independent reflections	<i>l</i> = -10 → 8

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0647P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.054$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	(Δ/σ) _{max} < 0.001
<i>S</i> = 1.00	$\Delta\rho_{\max} = 0.22 \text{ e } \text{Å}^{-3}$
2597 reflections	$\Delta\rho_{\min} = -0.21 \text{ e } \text{Å}^{-3}$
155 parameters	
H-atom parameters constrained	

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
N10–H1...O1 ⁱ	0.88	2.04	2.8747 (19)	157

Symmetry code: (i) 1 – *x*, –*y*, –*z*.

H atoms were treated as riding atoms (C–H = 0.95 and 0.98 Å, and N–H = 0.88 Å).

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1998); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 2
Comparison of selected bond lengths (Å) in some dipyrin-1-ones.

Compound	(III)	(IV)	(V)	(I)
Geometry	<i>Z-syn</i>	<i>Z-syn</i>	<i>Z-anti</i>	<i>Z-anti</i>
C4—C5	1.347 (10)	1.354 (1)	1.350 (3)	1.348 (2)
C5—C6	1.405 (10)	1.431 (1)	1.445 (3)	1.435 (2)
C1—N10 (N1)	1.380 (10)	1.353 (1)	1.376 (3)	1.370 (2)
C4—N10 (N1)	1.401 (10)	1.396 (1)	1.387 (3)	1.405 (2)
C9—N11 (N2)	1.362 (9)	1.354 (1)	1.362 (3)	1.359 (2)
C6—N11 (N2)	1.384 (9)	1.375 (1)	1.391 (3)	1.387 (2)
Reference	Cullen <i>et al.</i> (1977)	Cullen <i>et al.</i> (1979)	Cullen <i>et al.</i> (1979)	Present work

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA1085). Services for accessing these data are described at the back of the journal.

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