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# A novel class of fused heterocycles, benzo[*b*]furo[2,3-*c*]pyrroles

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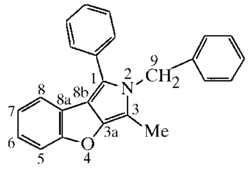
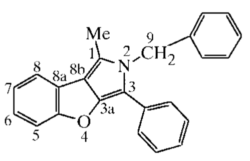
In the isomeric compounds 2-benzyl-3-methyl-1-phenylbenzo[*b*]furo[2,3-*c*]pyrrole and 2-benzyl-1-methyl-3-phenylbenzo[*b*]furo[2,3-*c*]pyrrole, both $C_{24}H_{19}NO$, the pyrrole ring, although presumably somewhat strained, does not differ appreciably from *N*-methylpyrrole except for a relatively short C—C single bond in the pyrrole ring.

## Comment

Fused heterocycles such as the title compounds, 2-benzyl-3-methyl-1-phenylbenzo[*b*]furo[2,3-*c*]pyrrole, (I), and 2-benzyl-1-methyl-3-phenylbenzo[*b*]furo[2,3-*c*]pyrrole, (II), are of great importance in the construction of more complex molecules, for example, by cycloaddition chemistry. In connection with our recent studies of these fused heterocycles, obtained by the reaction of mesoionic münchnones (1,3-oxazolium-5-olates) with 2-nitrobenzo[*b*]furan (Gribble *et al.*, 1998), we needed to differentiate the two isomeric compounds (I) and (II). The crystal structure determinations reported in the present paper support our isomer assignments reached using NMR techniques (Gribble *et al.*, 2000). The only previous example of the benzo[*b*]furo[2,3-*c*]pyrrole ring system was reported by Sha *et al.* (1995), but a crystal structure was not described.



(I)



(II)

The tricyclic fused benzofuropyrrole ring system in both (I) and (II) is planar, as expected. The C1 phenyl ring in (I) is twisted 37.3 (1)° out of planarity, while the corresponding C3 phenyl ring in (II) is twisted by 33.6 (1)°, consistent with the greater interaction of the C1 phenyl in (I) with H8. The *N*-benzyl phenyl rings in (I) and (II) are twisted 71.5 (6) and 79.4 (1)° out of the plane of the benzofuropyrrole ring system, respectively. This is anticipated, since $\pi$-conjugation between these aromatic systems is not possible.

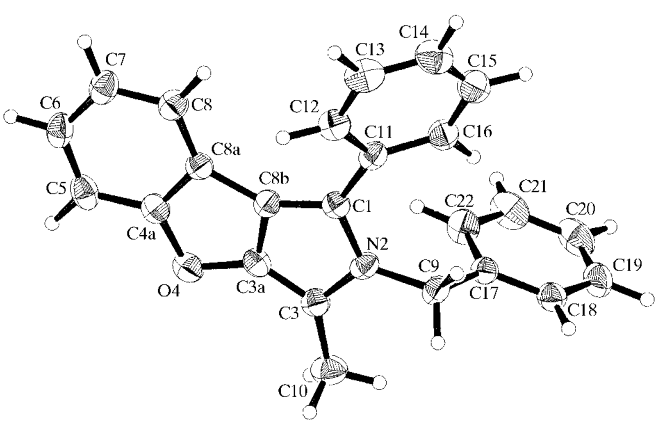


**Figure 1**
An *ORTEP* (Johnson, 1965) diagram of (I) showing 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

The unequal pyrrole C=C double bonds in (I) [C1—C8b 1.385 (6) Å and C3—C3a 1.353 (5) Å] and (II) [C1—C8b 1.385 (4) Å and C3—C3a 1.366 (4) Å] presumably reflect differing degrees of $\pi$-conjugation. For example, the larger C3—C3a bond length in (II) may be a consequence of $\pi$-conjugation in the benzofuran. Steric interaction on the C1—C8b bond, due to the phenyl ring in (I) or the methyl group in (II), appears minimal as the bond lengths are nearly identical [1.385 (6) Å in (I) and 1.385 (4) Å in (II)]. By comparison, *N*-methylpyrrole itself has a C=C double bond length of 1.35 Å and a C3—C4 bond length of 1.43 Å (electron diffraction; Vilkov *et al.*, 1962). On the other hand, *N*-benzylisoindole, which is a delocalized system like naphthalene, has an average pyrrole ring C=C double bond length of 1.384 Å (Bonnett *et al.*, 1985).

That pyrrole ring distortion is present in both (I) and (II) is evident from several bond angles. Thus, in (I) and (II) the C1—C8b—C8a bond angles are 147.2 (3)° and 147.7 (3)°, respectively, while the C3—C3a—O4 bond angles are 135.1 (4)° and 135.1 (3)°, respectively. The comparable bond angle in pyrrole itself (C2—C3—H3) is 126° (Vilkov *et al.*,

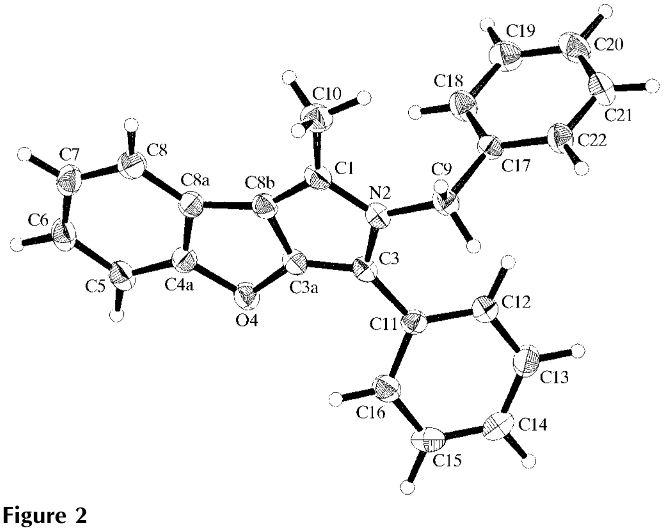


**Figure 2**
An *ORTEP* (Johnson, 1965) diagram of (II) showing 30% probability displacement ellipsoids. H atoms are drawn as spheres of arbitrary radii.

1962). Likewise, as a consequence of the two fused five-membered rings, the central C3a—C8b bond is very short for a C—C single bond in (I) and (II), at 1.394 (5) and 1.398 (4) Å, respectively. In *N*-methylpyrrole, the C3—C4 bond length is 1.43 Å (Vilkov *et al.*, 1962), and this single-bond length in *N*-benzylisoindole is 1.429 Å (Bonnett *et al.*, 1985). The C1—N2 and N2—C3 bond lengths in (I) and (II) are 1.389 (4) and 1.403 (6) Å, respectively, for (I) and 1.384 (3) and 1.408 (4) Å, respectively, for (II). These compare with the corresponding bond lengths in *N*-methylpyrrole (1.40 Å; Vilkov *et al.*, 1962) and *N*-benzylisoindole (1.362 Å; Bonnett *et al.*, 1985). The mean deviation of the pyrrole N2 atom from the plane of its nearest three neighbours, C1, C3 and C9, is −0.0095 Å in (I) and −0.0056 Å in (II). The internal bond angles in the pyrrole rings of (I) and (II) are quite similar to those found in *N*-benzylisoindole. For example, the C1—N2—C3 bond angles in (I) and (II) are 111.8 (3) and 111.6 (2)°, respectively. In *N*-benzylisoindole, this angle is 111° (Bonnett *et al.*, 1985). Likewise, the other internal pyrrole ring bond angles in (I) and (II) do not deviate much from those reported for *N*-benzylpyrrole. The least-squares planes mean deviation for the benzofuropyrrole ring is 0.0134 Å in (I) and 0.0086 Å in (II).

In summary, in compounds (I) and (II), which are reactive as dienes in Diels–Alder reactions, the pyrrole rings, although somewhat strained due to being fused to another five-membered ring, do not differ appreciably from *N*-methylpyrrole, except for a relatively short C—C single bond (C3a—C8b) in the pyrrole ring.

## Experimental

Compound (I) was prepared by our general method from 2-nitrobenzo[*b*]furan and *N*-benzyl-*N*-benzoylalanine (Gribble *et al.*, 1998), and recrystallized from acetone–petroleum ether to give rhomboidal crystals (m.p. 389–391 K). Compound (II) was prepared similarly from 2-nitrobenzo[*b*]furan and *N*-acetyl-*N*-benzyl-α-phenylglycine, and recrystallized from acetone–hexanes to give rhomboidal crystals (m.p. 426–427 K). The full synthetic details will be described separately (Gribble *et al.*, 2000).

### Compound (I)

*Crystal data*

$C_{24}H_{19}NO$
$M_r = 337.42$
Triclinic, $P\overline{1}$
$a = 10.405$ (2) Å
$b = 11.524$ (2) Å
$c = 9.177$ (2) Å
$\alpha = 113.44$ (1)°
$\beta = 113.94$ (2)°
$\gamma = 93.94$ (2)°
$V = 887.4$ (4) Å$^3$
$Z = 2$
$D_x = 1.263$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 20 reflections
$\theta = 6.3$–9.3°
$\mu = 0.077$ mm$^{-1}$
$T = 296.2$ K
Prism, light orange
0.4 × 0.3 × 0.2 mm

*Data collection*

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
4289 measured reflections
4067 independent reflections
1420 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.020$
$\theta_{\rm max} = 27.50$°
$h = 0 \rightarrow 13$
$k = -14 \rightarrow 14$
$l = -11 \rightarrow 10$
3 standard reflections every 150 reflections intensity decay: −0.6%

*Refinement*

Refinement on $F$
$R = 0.049$
$wR = 0.225$
$S = 1.030$
4067 reflections
236 parameters
H-atom parameters not refined; C—H 0.96–1.02 Å
$w = 1/[\sigma^2(F_o) + 0.00002|F_o|^2]$
$(\Delta/\sigma)_{\rm max} = 0.050$
$\Delta\rho_{\rm max} = 0.26$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.22$ e Å$^{-3}$
Extinction correction: Zachariasen (1967)
Extinction coefficient: 9.7 (7) × $10^{-7}$

### Compound (II)

*Crystal data*

$C_{24}H_{19}NO$
$M_r = 337.42$
Triclinic, $P\overline{1}$
$a = 9.956$ (1) Å
$b = 11.329$ (2) Å
$c = 8.939$ (2) Å
$\alpha = 109.89$ (1)°
$\beta = 107.06$ (1)°
$\gamma = 69.47$ (1)°
$V = 870.3$ (3) Å$^3$
$Z = 2$
$D_x = 1.287$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10.6$–17.1°
$\mu = 0.078$ mm$^{-1}$
$T = 296.2$ K
Prism, light brown
0.4 × 0.4 × 0.3 mm

*Data collection*

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: $\psi$ scan (North *et al.*, 1968)
$T_{\rm min} = 0.987$, $T_{\rm max} = 1.000$
4223 measured reflections
3991 independent reflections
1789 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.018$
$\theta_{\rm max} = 27.48$°
$h = 0 \rightarrow 12$
$k = -13 \rightarrow 14$
$l = -11 \rightarrow 11$
3 standard reflections every 150 reflections intensity decay: −1.4%

*Refinement*

Refinement on $F$
$R = 0.045$
$wR = 0.197$
$S = 1.040$
3991 reflections
236 parameters
H-atom parameters not refined; C—H 0.96–1.02 Å
$w = 1/[\sigma^2(F_o)]$
$(\Delta/\sigma)_{\rm max} = 0.050$
$\Delta\rho_{\rm max} = 0.24$ e Å$^{-3}$
$\Delta\rho_{\rm min} = -0.23$ e Å$^{-3}$
Extinction correction: Zachariasen (1967)
Extinction coefficient: 2.06 (7) × $10^{-6}$

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1994); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1997) and *DIRDIF*94 (Beurskens *et al.*, 1994); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); software used to prepare material for publication: *TEXSAN for Windows*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1233). Services for accessing these data are described at the back of the journal.

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