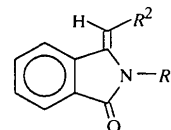


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palladium-catalyzed reaction between *N*-benzyl-*o*-iodobenzamide and phenylacetylene. We describe here the crystal structures of two additional examples, namely, (*Z*)-3-(*p*-methoxybenzylidene)isoindolin-1-one, (2), and (*Z*)-3-(2-hydroxy-2-methylpropylidene)-*N*-(*p*-tolyl)isoindolin-1-one, (3).



- (1) $R^1 = \text{CH}_2\text{Ph}$; $R^2 = \text{Ph}$
 (2) $R^1 = \text{H}$; $R^2 = \text{C}_6\text{H}_4\text{-}p\text{-OMe}$
 (3) $R^1 = \text{C}_6\text{H}_4\text{-}p\text{-Me}$; $R^2 = \text{CHC(OH)Me}_2$

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Two (*Z*)-3-aryl(alkyl)ideneisoindolin-1-ones

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Abstract

Two isoindolin-1-one derivatives, (*Z*)-3-(*p*-methoxybenzylidene)isoindolin-1-one [$\text{C}_{16}\text{H}_{13}\text{NO}_2$, (2)] and (*Z*)-3-(2-hydroxy-2-methylpropylidene)-*N*-(*p*-tolyl)isoindolin-1-one [$\text{C}_{19}\text{H}_{19}\text{NO}_2$, (3)], were synthesized by palladium-catalyzed hetero-annulation. The molecules of both compounds, which have a *Z* configuration, contain two planar parts, namely, the isoindolinone moiety and the phenyl ring. The r.m.s. deviation (0.111 Å) from the least-squares plane through the non-H atoms in compound (2) illustrates the overall molecular planarity. In (3), the phenyl ring is twisted out of the isoindolinone plane by 79.8 (1)°. Intermolecular hydrogen bonds link the molecules in (2) and (3) into infinite one-dimensional chains.

Comment

The isoindolinones (phthalamidines) form an important class of biologically important organic compounds (Fuska *et al.*, 1985) and exhibit a close structural similarity to bioactive indoles. As part of our on-going study of isoindolinone-containing heterocyclic systems of biological importance, we have reported recently the crystal structure of (*Z*)-*N*-benzyl-3-benzylideneisoindolin-1-one [(1); Khan *et al.*, 1998] prepared *via* a

The bond distances and angles observed in (2) and (3) are similar to those reported for substituted isoindoline structures (Khan *et al.*, 1998; McNab *et al.*, 1997; Barrett *et al.*, 1996; Feeder & Jones, 1996). The *Z* configurations of the molecules of (2) and (3), which contain essentially planar isoindolinone and phenyl moieties, are established by the torsion angle N—C8—C9—C10 of 0.6 (3)° in (2) and N—C7—C16—C17 of −2.7 (8)° in (3). The phenyl ring is twisted out of the isoindolinone plane (atoms C1—C8), with dihedral angles of 12.4 (1) and 79.8 (1)° in (2) and (3), respectively. The overall molecular planarity in (2) (r.m.s. deviation 0.111 Å) strongly suggests a resonance interaction extending over the C9 atom. This is reflected in a significant shortening of the C9—C10 bond length [1.437 (2) Å] in (2) compared with the C16—C17 bond [1.507 (4) Å] in (3) or with the expected $\text{C}_{\text{aryl}}\text{—C}_{\text{sp}^2}$ distance. The exocyclic bond angles around atoms C8 [in (2)] and C7 [in (3)] are highly asymmetric, with the N—C8—C9 [in (2)] and N—C7—C16 [in (3)] angles being markedly larger than the other angles. Intermolecular hydrogen bonds [N—

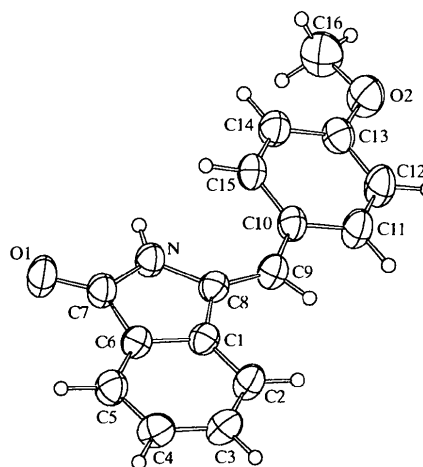


Fig. 1. ORTEPII (Johnson, 1976) view (50% probability level) of (2).

H1...O1(1-x, 1-y, -z) 2.877(2) Å in (2) and O2—H2O...O1(x+1, y, z) 2.850(3) Å in (3)] link the molecules into infinite one-dimensional chains.

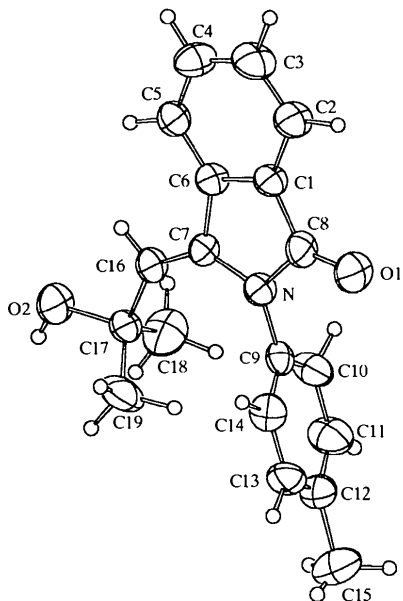


Fig. 2. ORTEP (Johnson, 1976) view (50% probability level) of (3).

Experimental

Compound (2) [m.p. 473 (1) K] was synthesized by stirring a mixture of *o*-iodobenzamide (1 mmol) and *p*-methoxyphenylacetylene (1.2 mmol) in DMF (5 ml) at 353 K for 16 h in the presence of bis(triphenylphosphine)palladium(II) chloride (3.5 mol%), cuprous iodide (8 mol%) and triethylamine (4 mmol) under a nitrogen atmosphere. After usual work-up and purification by chromatography (silica gel 60–80 mesh), the product obtained was cyclized to (2) by refluxing with sodium ethoxide in ethanol for 4 h. Compound (3) [m.p. 413 (1) K] was obtained by the reaction of *N-p*-tolyl-*o*-iodobenzamide and dimethylpropargyl alcohol in the presence of palladium and cuprous iodide catalysts as above by stirring at room temperature for 24 h. The crude product was cyclized with palladium acetate (5 mol%), LiCl (1 mmol) and K₂CO₃ (2.5 mmol) in DMF by stirring at 373 K for 16 h. Single crystals of (2) were obtained from ethanol/H₂O (1:1). For (3), isolation of single crystals was very difficult, but eventually crystals were obtained from ethanol solution; their quality was not as good as those of (2), which is reflected in the number of observed data [$I > 2\sigma(I)$], i.e. 31% in (3) compared with 85% in (2). The reason for the poor quality of single crystals of (3) is possibly the presence of the aliphatic side chain containing an OH group resulting in a very high solubility of the compound in almost all commonly used solvents.

Compound (2)

Crystal data

C₁₆H₁₃NO₂
M_r = 251.27

Cu Kα radiation
λ = 1.5418 Å

Monoclinic

$P2_1/n$
a = 13.130 (9) Å
b = 5.149 (2) Å
c = 18.166 (3) Å
β = 90.92 (3)°
V = 1228.0 (10) Å³
Z = 4
D_x = 1.359 Mg m⁻³
D_m not measured

Data collection

Enraf–Nonius CAD-4
diffractometer
ω–2θ scans
Absorption correction:
empirical (North *et al.*,
1968)
T_{min} = 0.782, T_{max} = 0.864
2499 measured reflections
2390 independent reflections

Refinement

Refinement on F²
R[F² > 2σ(F²)] = 0.049
wR(F²) = 0.121
S = 1.108
2390 reflections
172 parameters
H atoms not refined
w = 1/[σ²(F_o²) + (0.0671P)²
+ 0.306P]
where P = (F_o² + 2F_c²)/3

Table 1. Selected geometric parameters (Å, °) for (2)

N—C7	1.358 (2)	O2—C16	1.404 (3)
N—C8	1.400 (2)	C1—C8	1.451 (2)
O1—C7	1.225 (2)	C8—C9	1.335 (2)
O2—C13	1.345 (2)	C9—C10	1.437 (2)
C7—N—C8	113.1 (1)	N—C8—C1	104.7 (1)
C13—O2—C16	117.4 (2)	C8—C9—C10	132.7 (2)
O1—C7—N	126.0 (2)		
N—C8—C9—C10	0.6 (3)	C8—C9—C10—C11	−169.5 (2)
C1—C8—C9—C10	178.6 (2)	C16—O2—C13—C14	−13.6 (3)
C8—C9—C10—C15	11.2 (3)	C16—O2—C13—C12	167.3 (2)

Compound (3)

Crystal data

C₁₉H₁₉NO₂
M_r = 293.35
Triclinic
P1
a = 9.426 (2) Å
b = 9.795 (2) Å
c = 9.909 (2) Å
α = 68.70 (2)°
β = 81.17 (2)°
γ = 70.00 (2)°
V = 800.5 (3) Å³
Z = 2
D_x = 1.217 Mg m⁻³
D_m not measured

Cell parameters from 25 reflections

θ = 10–20°
μ = 0.726 mm⁻¹
T = 293 (2) K
Prism
0.40 × 0.30 × 0.20 mm
Colourless

2021 reflections with

$I > 2\sigma(I)$
R_{int} = 0.017
θ_{max} = 73.43°
h = 0 → 15
k = 0 → 6
l = −22 → 22
3 standard reflections
every 100 reflections
intensity decay: 2%

(Δ/σ)_{max} = −0.088
Δρ_{max} = 0.165 e Å⁻³
Δρ_{min} = −0.289 e Å⁻³
Extinction correction: none
Scattering factors from
International Tables for
Crystallography (Vol. C)

Mo Kα radiation

λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–16°
μ = 0.079 mm⁻¹
T = 293 (2) K
Prism
0.30 × 0.10 × 0.08 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\max} = 24.92^\circ$
ω - 2θ scans	$h = -10 \rightarrow 11$
Absorption correction: none	$k = 0 \rightarrow 11$
2771 measured reflections	$l = -10 \rightarrow 11$
2771 independent reflections	3 standard reflections
848 reflections with $I > 2\sigma(I)$	every 100 reflections intensity decay: 3%

Refinement

Refinement on F^2	$(\Delta/\sigma)_{\max} = 0.006$
$R[F^2 > 2\sigma(F^2)] = 0.055$	$\Delta\rho_{\max} = 0.194 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.104$	$\Delta\rho_{\min} = -0.225 \text{ e } \text{\AA}^{-3}$
$S = 1.272$	Extinction correction: none
2771 reflections	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)
202 parameters	
H atoms not refined	
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 2. Selected geometric parameters (\AA , $^\circ$) for (3)

O1—C8	1.221 (4)	N—C9	1.437 (4)
O2—C17	1.445 (4)	C1—C8	1.453 (5)
N—C8	1.387 (4)	C7—C16	1.336 (4)
N—C7	1.417 (4)	C16—C17	1.507 (4)
C8—N—C7	111.9 (3)	C7—C16—C17	139.7 (3)
N—C8—C1	106.5 (3)	O2—C17—C16	101.7 (3)
N—C7—C16—C17	-2.7 (8)	C7—C16—C17—O2	164.5 (5)
C9—N—C7—C16	7.4 (7)	C7—C16—C17—C19	48.2 (7)
C9—N—C8—O1	-6.2 (6)	C7—C16—C17—C18	-79.2 (6)

For both compounds, data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structures: *MULTAN88* (Debaerdemaeker *et al.*, 1988); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ZORTEP* (Zsolnai, 1995); software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA1225). Services for accessing these data are described at the back of the journal.

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2-tert-Butoxycarbonylamino-2-isopropyl-4-pentenamide, a new conformationally restricted α,α -dialkylglycine derivative†

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Abstract

The α -allyl- α -isopropylglycine derivative, $\text{C}_{13}\text{H}_{24}\text{N}_2\text{O}_3$, adopts a fully extended C_5 conformation. The φ and ψ torsion angles are close to the expected values of 180° . The amide $\text{C}=\text{O}$ group plays the role of a double acceptor, namely, of an intramolecular hydrogen bond with the urethane $\text{N}-\text{H}$ group, and of an intermolecular hydrogen bond with the amide $\text{N}-\text{H}$ group of a symmetry-related molecule ($2 - x, -y, -z$).

Comment

The incorporation of conformationally restricted residues, such as α,α -disubstituted amino acids, constitutes an important approach to studying the bioactive conformation of peptides, and also offers the potential to discover analogues with improved stability, bioselectivity and bioavailability. In this sense, α -allyl-substituted amino acids may not only be utilized to influence the local conformation of the peptide, but may also be used

† Alternative name: *tert*-butyl *N*-(1-aminocarbonyl-1-isopropylbut-3-enyl)carbamate.