Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

N-Benzyl-2′-iodocinnamanilide and *N*-benzyl-2′-iodo-4′-methyl-2-phenylcinnamanilide

S. Renganayaki,[a] E. Subramanian,[a] S. Shanmuga Sundara Raj[b] and Hoong-Kun Fun[b]*

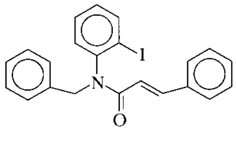
[a]Department of Crystallography and Biophysics, University of Madras, Guindy Campus, Chennai 600 025, India, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

Received 4 November 1999
Accepted 24 November 1999

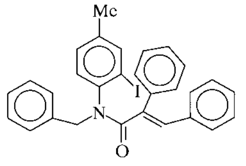
The aromatic ring of the cinnamic moiety in *N*-benzyl-2′-iodocinnamanilide, $C_{22}H_{18}INO$, (I), and *N*-benzyl-2′-iodo-4′-methyl-2-phenylcinnamanilide, $C_{29}H_{24}INO$, (II), makes a dihedral angle with the iodophenyl ring of 72.1 (2) and 81.0 (2)° in (I) and (II), respectively. In (I), molecules exist as discrete components, while in (II), they form infinite chains along the *b* axis, through I···O non-bonded interactions.

Comment

Cinnamoyl anilides are substrates for cyclization to biologically active five-membered 2-oxindole derivatives and six-membered 2-oxyquinolines by photochemical methods. *ortho*-Iodinated anilides are used for the same reaction by electrochemical methods. The interest lies in the synthetic potential of these iodinated compounds and those of other acyclamides, which react with a wide range of nucleophilic compounds and which therefore present new possibilities in the synthesis of heterocyclic compounds (Augustin *et al.*, 1980). We have undertaken X-ray structure analysis of *N*-benzyl-2′-iodocinnamanilide (I) and *N*-benzyl-2′-iodo-4′-methyl-2-phenylcinnamanilide (II) to identify conformational features that favour cyclization.



(I)



(II)

The molecular geometry of the cinnamamide part of the title compounds agrees well with their analogues, *N*-methyl-2′-nitrocinnamanilide (Subramanian *et al.*, 1999) and *N*-(4-chloro-2-iodophenyl)-*N*-methylcinnamamide (Renganayaki *et al.*, 1999), reported by our group, and with other reported values (Iwamoto & Kashino, 1990; Iwamoto *et al.*, 1989). The C—I distance [2.094 (4) in (I) and 2.101 (4) Å in (II)] is comparable with those reported in the literature (Elmali & Elerman, 1997; Banerjee *et al.*, 1994). Views of molecules (I) and (II) can be seen in Figs. 1 and 2, respectively.

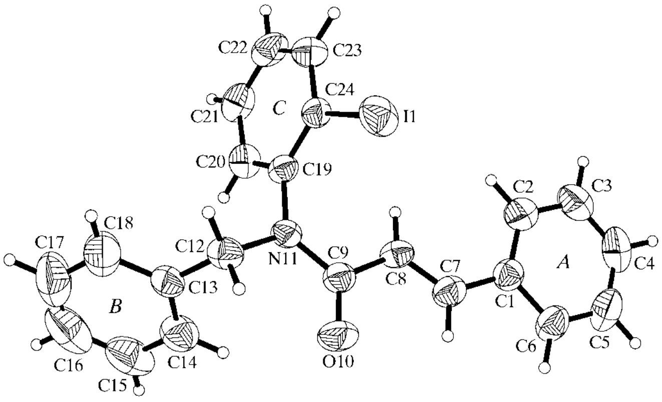


Figure 1
The structure of (I) showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

The widening of the C1—C7—C8 angle [128.1 (4)°] in (I) is attributable to steric factors involving C2 and C8 [C2···C8 = 3.040 (6) Å]. Steric repulsion between phenyl rings *A* and *D* in (II) might contribute to further widening of this angle [130.8 (4)°].

In both compounds, the phenylmethyl ring *B* and the carbonyl group are synperiplanar (*cis*) to each other [O10—C9—N11—C12 = 4.4 (6)° in (I) and 3.9 (6)° in (II)] and the phenyl ring *C* is antiperiplanar (*trans*) to the carbonyl group, with the O10—C9—N11—C19 torsion angle = −178.7 (4) in (I) and −177.7 (4)° in (II). As seen from the torsion angle, the α,β-unsaturated carbonyl unit has the *s-cis* conformation. The dihedral angles between rings are *A*/*B* 62.0 (3), *A*/*C* 72.1 (2) and *B*/*C* 60.7 (2) for (I), and 51.9 (3), 81.0 (2) and 48.0 (3)°, respectively, for (II). In (II), rings *C* and *D* are in a *syn* orientation, with an interplanar angle of 21.6 (2)°.

In (I), the packing of the molecules is stabilized by C—H···O and van der Waals interactions, while in (II) the

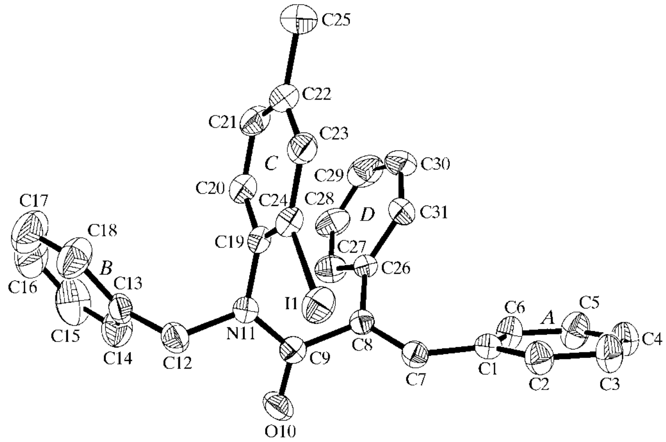


Figure 2
The structure of (II) showing 30% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

packing is also stabilized by additional I$\cdots$O interactions [I1$\cdots$O10$(-x+1, y+\frac{1}{2}, -z+\frac{1}{2})$ = 3.082 (3) Å].

Experimental

For the preparation of (I) the following procedure was employed. To a solution of *o*-iodoaniline (0.2 mol) and pyridine (0.2 mol) in dry benzene (50 ml), cinnamoyl bromide (0.2 mol in hexane) was added dropwise. The mixture was heated in a water bath at 333–343 K for 5 h and then poured into 80–100 ml of water. The benzene layer was separated and washed repeatedly with water (3–4 times). The benzene was dried with magnesium sulfate and then evaporated to obtain the anilide. For the benzylation of the anilide, NaH (0.2 mol) was taken in a round-bottomed flask. A solution of anilide (0.2 mol) in dry dimethylformamide (DMF; 50 ml) was added to the NaH. The reaction mixture was stirred for 15 min, and then benzyl bromide was added and stirred for 3 h. The reaction mixture was poured into water, extracted with ethyl acetate and washed with water repeatedly to remove the DMF, and the compound was recrystallized from dichloromethane. For the preparation of (II), the synthesis procedure was the same as for (I), with α-phenylcinnamoyl bromide as the starting material.

Compound (I)

Crystal data

$C_{22}H_{18}INO$
M_r = 439.27
Orthorhombic, *Pbca*
a = 17.7759 (3) Å
b = 9.0661 (2) Å
c = 23.5939 (3) Å
V = 3802.35 (12) Å^3
Z = 8
D_x = 1.535 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 8192 reflections
θ = 1.73–28.37°
μ = 1.693 mm^{-1}
T = 293 (2) K
Plate, colourless
0.28 × 0.14 × 0.06 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.721, T_{max} = 0.901
27 608 measured reflections
4666 independent reflections
2674 reflections with $I > 2\sigma(I)$
R_{int} = 0.06
θ_{max} = 28.31°
$h = -23 \rightarrow 13$
$k = -11 \rightarrow 12$
$l = -31 \rightarrow 30$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.095
S = 1.091
4666 reflections
226 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.023P)^2 + 2.0205P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −1.21 e Å^{-3}

Compound (II)

Crystal data

$C_{29}H_{24}INO$
M_r = 529.39
Monoclinic, $P2_1/c$
a = 10.8150 (2) Å
b = 11.3607 (2) Å
c = 20.2477 (5) Å
β = 91.271 (1)°
V = 2487.14 (9) Å^3
Z = 4
D_x = 1.414 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6014 reflections
θ = 1.88–28.32°
μ = 1.308 mm^{-1}
T = 293 (2) K
Block, colourless
0.32 × 0.18 × 0.10 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.674, T_{max} = 0.897
19 536 measured reflections
6131 independent reflections
2831 reflections with $I > 2\sigma(I)$
R_{int} = 0.093
θ_{max} = 28.53°
$h = -10 \rightarrow 14$
$k = -15 \rightarrow 14$
$l = -26 \rightarrow 21$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.057
$wR(F^2)$ = 0.102
S = 0.958
6131 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.028P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.79 e Å^{-3}

Table 1
Selected geometric parameters (Å) for (I).

I1—C24	2.094 (4)	N11—C19	1.434 (4)
C9—N11	1.360 (5)	N11—C12	1.479 (5)

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

I1—C24	2.101 (4)	N11—C19	1.426 (5)
C9—N11	1.370 (5)	N11—C12	1.478 (5)
C8—C7—C1	130.8 (4)	C7—C8—C26	125.8 (4)

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 1990).

The authors thank M. Raja, Scientist, SPIC Science Foundation, Chennai India, and Professor K. K. Balasubramanian, Indian Institute of Technology, Madras, for the synthesis and supply of the compounds. HKF thanks the Malaysian Government and Universiti Sains Malaysia for research grant R & D No. 305/pfizik/622004. SSSR thanks the Universiti Sains Malaysia for a Visiting Postdoctoral Fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1348). Services for accessing these data are described at the back of the journal.

References

Augustin, M., Richter, M. & Sala, S. (1980). *J. Prakt. Chem.* **332**, 55–68.
Banerjee, R., Das, K., Ganesh, V., Banerjee, P., Surolia, A. & Vijayan, M. (1994). *Acta Cryst.* C**50**, 1726–1728.
Elmali, A. & Elerman, Y. (1997). *Acta Cryst.* C**53**, 791–793.
Iwamoto, T. & Kashino, S. (1990). *Acta Cryst.* C**46**, 686–688.
Iwamoto, T., Kashino, S. & Haisa, M. (1989). *Acta Cryst.* C**45**, 1110–1112.
Renganayaki, S., Subramanian, E., Shanmuga Sundara Raj, S. & Fun, H.-K. (1999). *Acta Cryst.* C**55**, 1672–1673.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXTL*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.
Subramanian, E., Renganayaki, S., Shanmuga Sundara Raj, S. & Fun, H.-K. (1999). *Acta Cryst.* C**55**, 764–766.