

- Fink, H. & Stahl, I. (1985). *Acta Cryst.* **C41**, 151–153.
 Fu, T. Y., Leibovitch, M., Scheffer, J. R. & Trotter, J. (1997). *Acta Cryst.* **C53**, 1255–1256.
 Harms, K. (1993). *XCAD4. Program for the Reduction of CAD-4 Diffractometer Data*. University of Marburg, Germany.
 Juaristi, E., Tapia, J. & Mendez, R. (1986). *Tetrahedron*, **421**, 1253–1264.
 Juaristi, E., Valenzuela, B. A. & Valle, L. (1984). *J. Org. Chem.* **49**, 3026–3027.
 Kalf, H. T. & Romers, C. (1966). *Acta Cryst.* **20**, 490–496.
 Page, P. C. B., van Niel, M. B. & Westwood, D. (1988). *J. Chem. Soc. Perkin Trans. 1*, pp. 269–275.
 Page, P. C. B., Wilkes, R. D., Namwindwa, E. S. & Witty, M. J. (1996). *Tetrahedron*, **52**, 2125–2154.
 Romers, C., Altona, C., Buys, H. R. & Havinga, E. (1969). *Top. Stereochem.* **4**, 39–97.
 Seebach, D. & Corey, E. J. (1975). *J. Org. Chem.* **40**, 231–237.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.
 Walker, N. & Stuart, D. (1983). *Acta Cryst.* **A39**, 158–166.
 Zsolnai, L. (1993). *ZORTEP. Program for Graphic Representation of Crystal Structures*. University of Heidelberg, Germany.

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N-Benzyl-*N*-(2-iodo-4-methylphenyl)-cinnamamide and *N*-benzyl-*N*-(*p*-tolyl)-cinnamamide

S. SHANMUGA SUNDARA RAJ,^a S. RENGANAYAKI,^b
 E. SUBRAMANIAN^b AND HOONG-KUN FUN^a

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

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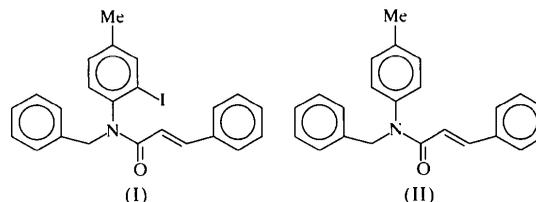
Abstract

The cinnamamide moiety in the crystals of the title compounds, C₂₃H₂₀INO, (I), and C₂₃H₂₁NO, (II), is almost planar and the benzyl ring is twisted through 60.4(4) and 63.6(1)° with respect to this moiety in (I) and (II), respectively. In the unit cell, the molecules exist as dimers joined through C—H···O hydrogen bonding.

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. Interest lies in the

synthetic potential of the title iodinated compound, *N*-benzyl-*N*-(2-iodo-4-methylphenyl)cinnamamide, (I), 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 the X-ray structure analyses of the two title compounds, (I) and *N*-benzyl-*N*-(*p*-tolyl)cinnamamide, (II), as an extension of studies of the molecular packing of cinnamamide derivatives.



The bond lengths and angles of the cinnamamide group in (I) and (II) are comparable with the analogues *N*-methyl-2'-nitrocinnamamide (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 in (I) is comparable with the values of the *para*-substituted compounds [2.088(4) (Elmali & Elerman, 1997) and 2.085(4) Å (Banerjee *et al.*, 1994)]. The widening of the C1—C7—C8 angle [127.8(3)° in (I) and 128.5(3)° in (II)] is due to the intramolecular repulsion of C2 and C8 [C2···C8 = 3.034(5) Å in (I) and 3.045(4) Å in (II)] and perhaps also to the attractive intramolecular force between C7 and O10 [C7···O10 = 2.818(5) in (I) and 2.788(3) Å in (II)]. Structural studies reveal that the exocyclic N11 atom is *sp*² hybridized despite forming three valence bonds. The inner angle at C22 is smaller [C21—C22—C23: 118.6(3)° in (I) and 117.1(3)° in (II)] than the *sp*² angle commonly observed at methyl-substituted C-atom positions (Dominicano *et al.*, 1975).

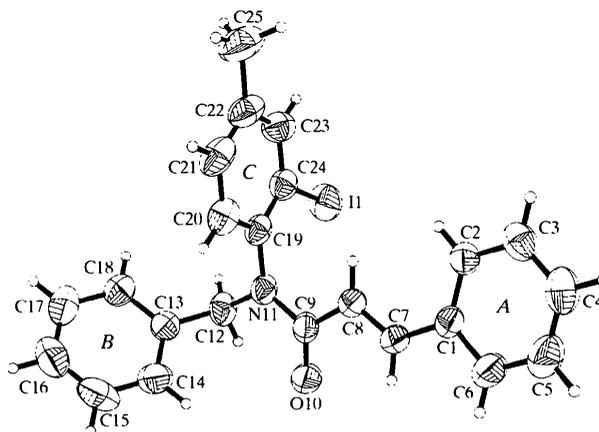


Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as spheres of arbitrary radii.

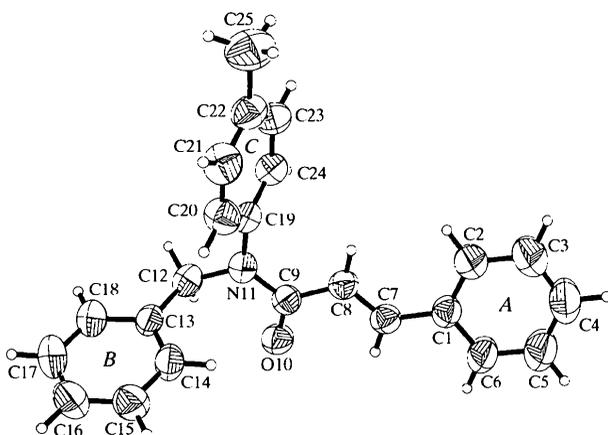


Fig. 2. The structure of (II) showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are shown as spheres of arbitrary radii.

In line with the thinking that hydrogen bonds are directional and electrostatic, the iodinated compound (I) appears to have a tendency to form a dimer, even though the $\text{H}\cdots\text{O}$ distance is larger [$\text{C17}\cdots\text{O10}^i = 3.549(5) \text{ \AA}$, $\text{H17A}\cdots\text{O10}^i = 2.838(3) \text{ \AA}$ and $\text{C17}-\text{H17A}\cdots\text{O10}^i = 134.2(3)^\circ$; symmetry code: (i) $x + 1, y, z$] than is usually observed in such bonds. In (II), the molecules also exist as dimers through $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonding between C7 and $\text{O10}(-x, 1 - y, -z)$, with a $\text{C7}\cdots\text{O10}$ distance of $3.370(3) \text{ \AA}$. Atoms of the dimer involved in the loop formed by the hydrogen bonds all lie in almost the same plane, with a maximum deviation of $0.10(3) \text{ \AA}$ for O10. An inversion centre relates the two molecules and lies in the plane of the dimer.

In both compounds, the benzyl ring B and the carbonyl group are synperiplanar (*cis*) to each other [$\text{O10}-\text{C9}-\text{N11}-\text{C12} = -2.4(5)^\circ$ in (I) and $-4.7(4)^\circ$ in (II)] and phenyl ring C is antiperiplanar (*trans*) to the carbonyl group [$\text{O10}-\text{C9}-\text{N11}-\text{C19} = 175.3(3)^\circ$ in (I) and $-179.5(2)^\circ$ in (II)]. As seen from the torsion angle, the α,β -unsaturated carbonyl unit has the *S-cis* conformation. The dihedral angles between rings A, B and C are A/B $60.4(4)$, A/C $85.0(1)$ and B/C $53.5(1)^\circ$ for (I), and $63.6(1)$, $73.1(1)$ and $87.6(1)^\circ$ for (II), respectively.

Experimental

For the preparation of (I), cinnamoyl chloride (0.2 mol in hexane) was added dropwise to a solution of *ortho*-iodotoluidine (0.2 mol) in dry benzene (50 ml) and pyridine (0.2 mol). The mixture was heated in a water bath at 333–343 K for 5 h and then the mixture was poured into water (80–100 ml). The benzene layer was separated and washed with water 3–4 times, then dried with magnesium sulfate and evaporated to obtain the anilide. For the benzylation of the anilide, NaH (0.2 mol) was placed in a round-bottomed flask. A solution of anilide (0.2 mol) in dry dimethylformamide (DMF, 50 ml) was added dropwise to the NaH. The reaction

mixture was stirred for 15 min, and then benzyl bromide was added and stirring continued for a further 3 h. The reaction mixture was poured into water and extracted with ethyl acetate and then washed with water repeatedly to remove the DMF. The compound was recrystallized from dichloromethane. For the preparation of (II), the synthetic procedure was the same as for (I), using the appropriate starting material (toluene).

Compound (I)

Crystal data

$\text{C}_{23}\text{H}_{20}\text{INO}$
 $M_r = 453.30$
 Triclinic
 $P\bar{1}$
 $a = 9.3376(4) \text{ \AA}$
 $b = 10.1794(4) \text{ \AA}$
 $c = 10.9289(5) \text{ \AA}$
 $\alpha = 95.498(1)^\circ$
 $\beta = 103.262(1)^\circ$
 $\gamma = 90.284(1)^\circ$
 $V = 1006.06(7) \text{ \AA}^3$
 $Z = 2$
 $D_x = 1.496 \text{ Mg m}^{-3}$
 D_m not measured

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scan
 Absorption correction: empirical (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.51, T_{\max} = 0.81$
 7002 measured reflections
 4807 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.119$
 $S = 1.037$
 4807 reflections
 235 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0501P)^2 + 0.7590P]$
 where $P = (F_o^2 + 2F_c^2)/3$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 4581 reflections
 $\theta = 1.92-28.32^\circ$
 $\mu = 1.602 \text{ mm}^{-1}$
 $T = 293(2) \text{ K}$
 Slab
 $0.48 \times 0.44 \times 0.14 \text{ mm}$
 Pale yellow

3598 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 28.28^\circ$
 $h = -12 \rightarrow 12$
 $k = -13 \rightarrow 12$
 $l = -14 \rightarrow 10$
 Intensity decay: negligible

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.17 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.99 \text{ e \AA}^{-3}$
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters ($\text{\AA}, ^\circ$) for (I)

C11—C24	2.100(3)	C9—N11	1.363(4)
C1—C7	1.463(5)	N11—C19	1.436(4)
C7—C8	1.319(5)	N11—C12	1.475(4)
C8—C9	1.486(4)	C22—C25	1.519(6)
C9—O10	1.228(4)		
C8—C7—C1	127.8(3)	C9—N11—C12	120.3(3)
C9—N11—C19	123.1(3)	C19—N11—C12	116.6(3)

Compound (II)

Crystal data

$\text{C}_{23}\text{H}_{21}\text{NO}$
 $M_r = 327.41$

Mo $K\alpha$ radiation
 $\lambda = 0.71073 \text{ \AA}$

Monoclinic

$P2_1/n$
 $a = 15.1665$ (16) Å
 $b = 6.2451$ (6) Å
 $c = 19.946$ (2) Å
 $\beta = 99.650$ (2)°
 $V = 1862.5$ (3) Å³
 $Z = 4$
 $D_x = 1.168$ Mg m⁻³
 D_m not measured

Cell parameters from 4298 reflections
 $\theta = 1.57$ – 27.50 °
 $\mu = 0.071$ mm⁻¹
 $T = 293$ (2) K
 Block
 $0.30 \times 0.14 \times 0.12$ mm
 Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
 ω scans
 Absorption correction: none
 10 485 measured reflections
 3221 independent reflections
 1705 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.093$
 $\theta_{\text{max}} = 25$ °
 $h = -18 \rightarrow 17$
 $k = -5 \rightarrow 7$
 $l = -23 \rightarrow 23$
 Intensity decay: negligible

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.068$
 $wR(F^2) = 0.157$
 $S = 1.036$
 3221 reflections
 227 parameters
 H atoms constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0606P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.24$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.24$ e Å⁻³
 Extinction correction:
SHELXTL (Sheldrick, 1997)
 Extinction coefficient:
 0.011 (2)
 Scattering factors from
International Tables for Crystallography (Vol. C)

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

C1—C7	1.461 (3)	C9—N11	1.374 (3)
C7—C8	1.323 (3)	N11—C19	1.434 (3)
C8—C9	1.471 (3)	N11—C12	1.465 (3)
C9—O10	1.225 (3)	C22—C25	1.510 (4)
C8—C7—C1	128.5 (3)	C9—N11—C12	117.5 (2)
C9—N11—C19	125.2 (2)	C19—N11—C12	117.1 (2)

Table 3. Hydrogen-bonding geometry (Å, °) for (II)

D—H...A	D—H	H...A	D...A	D—H...A
C7—H7A...O10 ⁱ	0.93	2.51	3.370 (3)	154

Symmetry code: (i) $-x, 1 - y, -z$.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structures: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structures: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PARST* (Nardelli, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1216). 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., Suroliya, A. & Vijayan, M. (1994). *Acta Cryst.* **C50**, 1726–1728.
 Dominicano, A., Vacigago, A. & Coulson, C. A. (1975). *Acta Cryst.* **B31**, 221–224.
 Elmali, A. & Elerman, Y. (1997). *Acta Cryst.* **C53**, 791–793.
 Iwamoto, T. & Kashino, S. (1990). *Acta Cryst.* **C46**, 686–688.
 Iwamoto, T., Kashino, S. & Haisa, M. (1989). *Acta Cryst.* **C45**, 1110–1112.
 Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
 Renganayaki, S., Subramanian, E., Shanmuga Sundara Raj, S. & Fun, H.-K. (1999). *Acta Cryst.* **C55**, 1672–1673.
 Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction of Area Detector Data*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). *SHELXTL. Software Reference Manual*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
 Siemens (1996). *SMART and SAINT. Area Detector Control and Integration Software*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
 Subramanian, E., Renganayaki, S., Shanmuga Sundara Raj, S. & Fun, H.-K. (1999). *Acta Cryst.* **C55**, 764–766.

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rac-5,5'-Bis(2-acetoxypopyl)-2,2'-fural

CARSTEN HANDROSCH, FRANK W. HEINEMANN AND HORST KISCH

Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstraße 1, D-91058 Erlangen, Germany.
E-mail: kisch@anorganik.chemie.uni-erlangen.de

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Abstract

The title compound, 2,2'-fural-5,5'-diyldi-prop-2-yl diacetate, C₂₀H₂₂O₈, lies about an inversion centre and forms a ladder-like structure wherein the furil backbone builds the steps which are then connected to each other by hydrogen-bond bridges (O...H distance 2.64 Å) between the side groups. The furan rings of neighbouring molecules are coplanar, with an interfacial distance of 3.65 Å.

Comment

The title compound, (I), was synthesized from *rac*-5-(2-acetoxypopyl)-2-furancarbaldehyde, a key intermediate in the total synthesis of the macrotretrolid Nonactin