

Acta Crystallographica Section C

**Crystal Structure
Communications**

ISSN 0108-2701

4,5-Dichlorophthalic acid–*trans*-cinnamamide (1/2) and 3,4,5,6-tetrachlorophthalic acid–*trans*-cinnamamide (1/2)

Hosomi, Ohba and Ito

Electronic paper

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

© 2000 International Union of Crystallography • Printed in Great Britain – all rights reserved

4,5-Dichlorophthalic acid–*trans*-cinnamamide (1/2) and 3,4,5,6-tetrachlorophthalic acid–*trans*-cinnamamide (1/2)

Hiroyuki Hosomi,^a Shigeru Ohba^{a*} and Yoshikatsu Ito^b

^aDepartment of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223-8522, Japan, and ^bDepartment of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan
Correspondence e-mail: ohba@chem.keio.ac.jp

Received 8 September 2000

Accepted 27 September 2000

Data validation number: IUC0000270

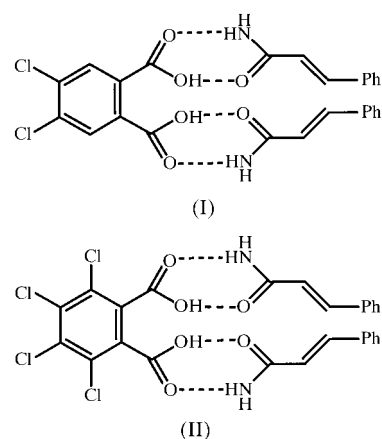
In the two title adducts, $C_8H_4Cl_2O_4 \cdot 2C_9H_9NO$ and $C_8H_2Cl_4O_4 \cdot 2C_9H_9NO$, respectively, the dicarboxylic acid is connected to two cinnamamide molecules through cyclic hydrogen bonds. The arrangement of the C=C bonds of neighbouring cinnamamide molecules is twisted.

Comment

The [2+2] photodimerization of *trans*-cinnamamides exclusively produces the α -type photodimer (Hung *et al.*, 1972). Photolysis of cocrystals of *trans*-cinnamamide with dicarboxylic acids have been investigated (Ito *et al.*, 2000). The main photoproduct was the β -dimer of cinnamamide for phthalic acid bis(*trans*-cinnamamide). However, the arrangement of the C=C bond between the neighbouring cinnamamide molecules is twisted and not suitable for [2+2] photodimerization. A pedal-like conformational change before photodimerization is expected.

The C=C bond axes of the neighbouring cinnamamide molecules adopt a twisted arrangement in both (I) and (II), as observed in the cocrystals with phthalic acid. The distance between the centres of the C20=C21 and C29=C30 bonds is 4.453 (4) Å in (I), and that for the C22=C23 and C31=C32 bonds is 4.146 (4) Å in (II). The hydrogen-bond networks in (I) and (II) are similar to one another. Both H atoms of the NH₂ groups are involved in the N—H...O hydrogen bonds to form a two-dimensional sheet.

Powdered crystals were spread between two Pyrex plates and irradiated with a 400 W high-pressure mercury lamp for 20 h under an argon stream at room temperature. The yields of β -dimer of cinnamamide from (I) and (II) were estimated by thin-layer chromatography and NMR spectra to be 31 and 19%, respectively.



Experimental

All the compounds were commercially available. Crystals were grown by slow evaporation from 2-propanol solution of the mixture of dichloro- or tetrachlorophthalic acid and *trans*-cinnamamide (1:2).

Compound (I)

Crystal data

$C_8H_4Cl_2O_4 \cdot 2C_9H_9NO$
 $M_r = 529.38$
Triclinic, $P1$
 $a = 9.6821$ (7) Å
 $b = 18.4661$ (12) Å
 $c = 7.4203$ (5) Å
 $\alpha = 93.611$ (5)°
 $\beta = 105.676$ (5)°
 $\gamma = 100.636$ (5)°
 $V = 1246.4$ (2) Å³

$Z = 2$
 $D_x = 1.410$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 14.3$ – 15.0 °
 $\mu = 0.305$ mm⁻¹
 $T = 298$ (1) K
Plate, colourless
0.70 × 0.40 × 0.15 mm

Data collection

Rigaku AFC-7R diffractometer
 θ - 2θ scans
Absorption correction: ψ scan
(North *et al.*, 1968)
 $T_{min} = 0.745$, $T_{max} = 0.955$
6174 measured reflections
5732 independent reflections
4328 reflections with $I > 2\sigma(I)$

$R_{int} = 0.013$
 $\theta_{max} = 27.5$ °
 $h = -13 \rightarrow 13$
 $k = -24 \rightarrow 24$
 $l = -10 \rightarrow 0$
3 standard reflections every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.047$
 $wR(F^2) = 0.198$
 $S = 1.28$
5732 reflections
413 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.10P)^2 + 0.30P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.48$ e Å⁻³
 $\Delta\rho_{min} = -0.37$ e Å⁻³

Table 1

Selected geometric parameters (Å) for (I).

C11—C15	1.720 (3)	O8—C28	1.251 (3)
C12—C14	1.731 (3)	N9—C19	1.331 (4)
O3—C11	1.204 (3)	N10—C28	1.322 (3)
O4—C11	1.317 (3)	C19—C20	1.482 (4)
O5—C18	1.307 (3)	C20—C21	1.298 (4)
O6—C18	1.206 (3)	C28—C29	1.481 (4)
O7—C19	1.252 (3)	C29—C30	1.315 (3)

Table 2

Hydrogen-bonding geometry (Å, °) for (I).

<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>
O4—H4···O7	0.83 (4)	1.78 (4)	2.553 (3)	155 (5)
O5—H5···O8	0.84 (4)	1.69 (4)	2.491 (3)	158 (4)
N9—H9A···O3	1.06 (3)	1.86 (3)	2.905 (4)	168 (5)
N9—H9B···O8 ⁱ	0.87 (4)	2.35 (5)	3.081 (3)	142 (5)
N10—H10A···O6	1.01 (4)	1.94 (4)	2.923 (3)	165 (3)
N10—H10B···O7 ⁱⁱ	0.78 (4)	2.27 (4)	3.039 (3)	175 (4)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1-x, -y, 1-z$.

Compound (II)

Crystal data

$C_8H_2Cl_4O_4 \cdot 2C_9H_9NO$

$M_r = 598.27$

Triclinic, $P\bar{1}$

$a = 9.937$ (2) Å

$b = 15.895$ (4) Å

$c = 9.015$ (2) Å

$\alpha = 93.48$ (2)°

$\beta = 110.57$ (1)°

$\gamma = 91.58$ (2)°

$V = 1328.8$ (5) Å³

$Z = 2$

$D_x = 1.495$ Mg m⁻³

Mo $K\alpha$ radiation

Cell parameters from 25 reflections

$\theta = 14.4$ – 15.0 °

$\mu = 0.490$ mm⁻¹

$T = 298$ (1) K

Plate, colourless

$0.60 \times 0.60 \times 0.15$ mm

Data collection

Rigaku AFC-7R diffractometer

θ – 2θ scans

Absorption correction: ψ scan

(North *et al.*, 1968)

$T_{\min} = 0.772$, $T_{\max} = 0.929$

6442 measured reflections

6092 independent reflections

4659 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$

$\theta_{\text{max}} = 27.5$ °

$h = -13 \rightarrow 0$

$k = -21 \rightarrow 21$

$l = -12 \rightarrow 12$

3 standard reflections

every 150 reflections

intensity decay: none

Refinement

Refinement on F^2

$R(F) = 0.038$

$wR(F^2) = 0.113$

$S = 1.06$

6092 reflections

423 parameters

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 0.6677P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.27$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 3

Selected geometric parameters (Å) for (II).

Cl1—Cl8	1.722 (2)	O9—C21	1.249 (3)
Cl2—Cl7	1.720 (3)	O10—C30	1.265 (3)
Cl3—Cl6	1.718 (2)	N11—C21	1.313 (3)
Cl4—Cl5	1.725 (2)	N12—C30	1.306 (3)
O5—C13	1.208 (2)	C21—C22	1.472 (4)
O6—C13	1.312 (2)	C22—C23	1.311 (3)
O7—C20	1.294 (2)	C30—C31	1.467 (3)
O8—C20	1.210 (2)	C31—C32	1.326 (3)

Table 4

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

<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>
O6—H6···O9	0.93 (4)	1.68 (4)	2.575 (3)	163 (3)
O7—H7···O10	1.03 (4)	1.43 (4)	2.444 (2)	167 (4)
N11—H11A···O5	0.81 (3)	2.15 (3)	2.949 (3)	169 (3)
N11—H11B···O7 ⁱ	0.89 (4)	2.23 (4)	3.120 (3)	177 (3)
N12—H12A···O8	0.88 (3)	1.97 (3)	2.835 (3)	166 (2)
N12—H12B···O9 ⁱⁱ	0.88 (3)	2.14 (3)	3.001 (2)	167 (3)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, -y, -z$.

The refined bond distances involving the H atoms are 0.78 (4)–1.06 (5) and 0.81 (3)–1.03 (4) Å for (I) and (II), respectively.

For both compounds, data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *TEXSAN*.

The authors thank Mr Akihiro Kondo for preparing the title crystals.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Hung, J. D., Lahav, M., Luwisch, M. & Schmidt, G. M. J. (1972). *Isr. J. Chem.* **10**, 585–599.
- Ito, Y., Hosomi, H. & Ohba, S. (2000). *Tetrahedron*. In the press.
- Molecular Structure Corporation (1993). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1999). *TEXSAN*. Version 1.10. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.