Data collection

Enraf–Nonius CAD-4 diffractometer
ω–2θ scans
Absorption correction: none
2765 measured reflections
2606 independent reflections
2267 reflections with $I > 3\sigma(I)$
$R_{\rm int} = 0.0179$

$\theta_{\rm max} = 24.97°$
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 16$
$l = -14 \rightarrow 13$
2 standard reflections every 100 reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0502$
$wR(F^2) = 0.1337$
$S = 1.088$
2606 reflections
272 parameters
H atoms refined isotropically
$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2 + 1.1547P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.656$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.188$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

S—C10	1.763 (3)	C2—C1	1.519 (4)
S—C2	1.839 (3)	C2—C3	1.518 (4)
O1—C9	1.381 (3)	C9—C8	1.373 (4)
O1—C1	1.408 (4)	C8—C3	1.495 (4)
O2—C3	1.189 (4)	C17—C18	1.282 (6)
C10—S—C2	108.93 (12)	O1—C9—C7	115.1 (3)
C9—O1—C1	114.0 (2)	O2—C3—C8	122.7 (3)
C1—C2—C3	110.7 (2)	O2—C3—C2	122.3 (3)
O1—C1—C2	113.7 (2)	C8—C3—C2	115.0 (2)
C8—C9—O1	124.1 (3)		
C10—S—C2—C16	170.2 (2)	O1—C9—C8—C3	−2.9 (4)
C9—O1—C1—C2	50.9 (3)	C9—C8—C3—C2	−1.4 (4)
C3—C2—C1—O1	−53.5 (4)	S—C2—C3—O2	83.4 (3)
C16—C2—C1—O1	−177.5 (3)	C1—C2—C3—C8	27.7 (3)
C1—O1—C9—C8	−22.3 (4)	C3—C2—C16—C17	−63.0 (4)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

The authors wish to thank the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Madras, India, for data collection and Professor K. K. Balasubramanian, Department of Chemistry, Indian Institute of Technology, Madras, India, for helpful discussions.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: VJ1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 794–797

Two Monoclinic Forms of Diclofenac Acid

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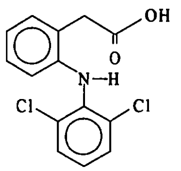
(*Received 21 November 1996; accepted 3 February 1997*)

Abstract

Diclofenac acid, [2-(2,6-dichlorophenylamino)phenyl]-acetic acid, $C_{14}H_{11}Cl_2NO_2$, crystallizes in two polymorphic forms in the monoclinic system. In both forms, molecules are linked to each other through the carboxyl groups giving rise to centrosymmetric dimers. No interaction among different dimers has been found.

Comment

The crystal structure determination of diclofenac acid (HD) is part of our structural studies on non-steroidal anti-inflammatory agents (Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996, 1997). In this paper we describe the X-ray crystal and molecular structures of two monoclinic forms of diclofenac acid, namely, HD1 (space group $P2_1/c$) and HD2 (space group $C2/c$). The crystal data of HD2 have been



HD1/HD2

published previously (Moser, Sallmann & Weisenberg, 1990; Kovala-Demertzi, Mentzafos & Terzis, 1993), but no detailed structure analysis was reported.

In both forms, the molecules form centrosymmetric dimers linked by hydrogen bonds between the carboxylic O atoms. The structure of the dimeric unit of HD1 is reported in Fig. 1. The dimers are packed in such a way that no strong interaction arises among them. The N—H group is located in a sterically hindered position and does not participate in intermolecular hydrogen bonds. On the contrary, as observed in diclofenac salts (Castellari & Sabatino, 1994, 1996; Castellari & Ottani, 1995, 1996, 1997), it originates a bifurcate intramolecular hydrogen bond interacting with the adjacent acceptor atoms Cl1 and O1 (Tables 2 and 4). The two forms are very closely related, differing significantly only in the geometry of the carboxylic group, with the largest differences occurring in the C—O bond lengths and in the values of the C—C—C—O torsion angles. A more effective π-electron delocalization is observed in the carboxylic group of HD1 [C14—O1 1.233 (3) and C14—O2 1.289 (3) Å] with respect to HD2 [C14—O1

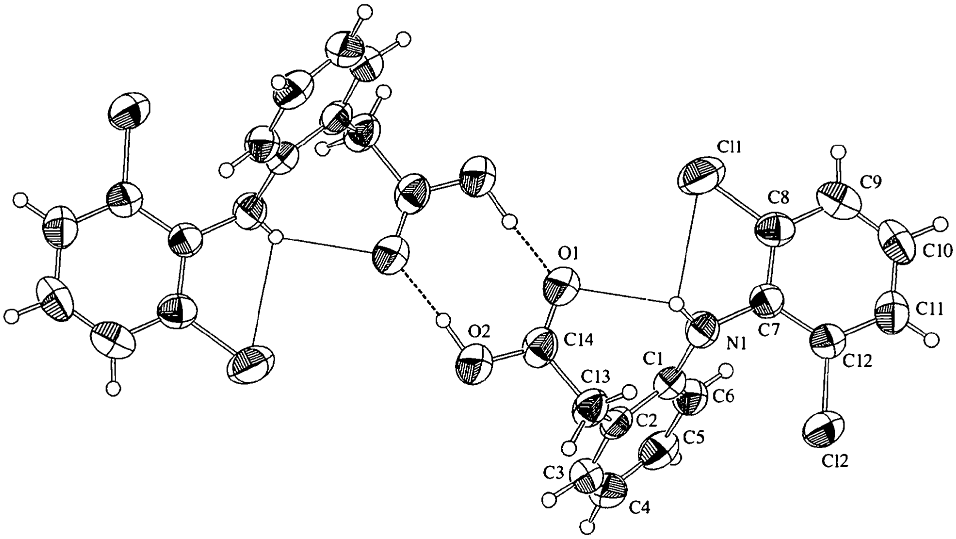


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of the HD1 dimer showing the atom labelling. Intramolecular hydrogen bonds are indicated by light lines, whereas dashed light lines have been used for intermolecular hydrogen bonds. Atoms are represented by displacement ellipsoids of 50% probability. [Symmetry code for the unlabelled molecule: $-x$, $-y$, $-z$.]

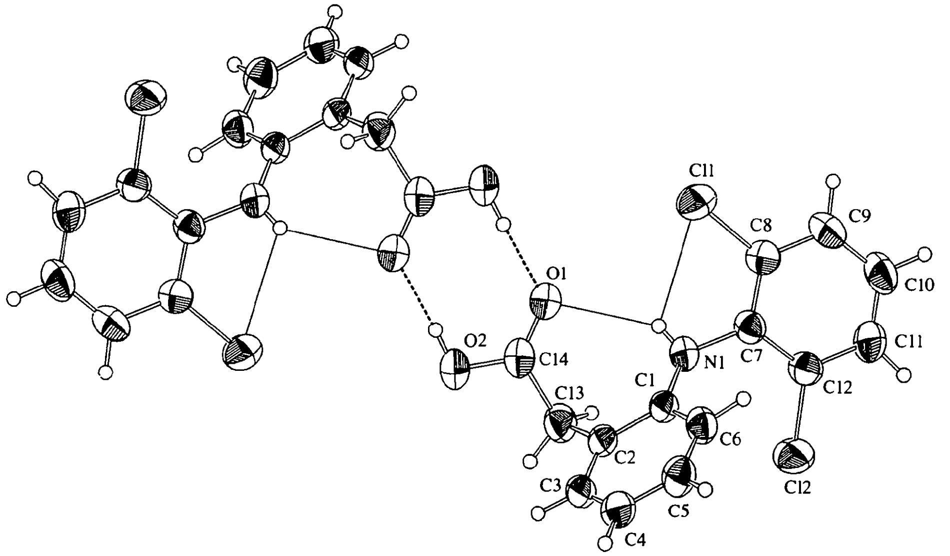


Fig. 2. *ORTEP*II (Johnson, 1976) diagram of the HD2 dimer showing the atom labelling. Intramolecular hydrogen bonds are indicated by light lines, whereas dashed light lines have been used for intermolecular hydrogen bonds. Atoms are represented by displacement ellipsoids of 50% probability. [Symmetry code for the unlabelled molecule: $\frac{1}{2} - x$, $-y - \frac{1}{2}$, $-z$.]

1.216 (2), C14—O2 1.304 (2) Å] and the torsion angle C2—C13—C14—O2 is 96.3 (3) in HD1 and 109.4 (2)° in HD2. Also, the O—H and O···O distances [1.07 (4) and 1.56 (4) in HD1, and 0.87 (4) and 1.77 (3) Å in HD2] reflect more delocalized OCO π-electrons in HD1. The angles between the least-squares planes of the two aromatic rings are 70.00 (9) and 69.28 (8)° for HD1 and HD2, respectively. In both forms, the amine moiety (N1, C1, C7, H1) is pyramidal, with the N atom out of the C1, C7, H1 plane by 0.195 (2) in HD1 and 0.187 (2) Å in HD2. Inspection of density values shows that HD2 gives a more efficient crystal packing (D_x 1.477 against 1.454 Mg m^{-3} in HD1), which corresponds also to a more asymmetric hydrogen bridge.

Experimental

Diclofenac sodium salt (Sigma, St. Louis, USA) was dissolved in water. The solution was acidified with HCl (37%; Merck, Darmstad, Germany). The resulting powders were filtered, washed with water and dried *in vacuo*. Recrystallization of HD1 was from methanol by slow evaporation. Crystals of HD2 were obtained by slow diffusion of an acetone solution in *n*-hexane.

Compound HD1

Crystal data

$C_{14}H_{11}Cl_2NO_2$
$M_r = 296.14$
Monoclinic
$P2_1/c$
$a = 8.384\ (2)$ Å
$b = 10.898\ (2)$ Å
$c = 14.822\ (5)$ Å
$\beta = 92.76\ (2)°$
$V = 1352.7\ (6)$ Å^3
$Z = 4$
$D_x = 1.454$ Mg m^{-3}
$D_m = 1.45$ Mg m^{-3}
D_m measured by flotation in a 1-bromo-3-chloropropane/*p*-xylene mixture

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7–12°$
$\mu = 0.476$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.40 × 0.15 × 0.10 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω scans
Absorption correction: none
4079 measured reflections
3940 independent reflections
1597 reflections with $I > 2\sigma(I)$

$R_{int} = 0.0374$
$\theta_{max} = 29.98°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 15$
$l = 0 \rightarrow 20$
3 standard reflections
frequency: 160 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0397$
$wR(F^2) = 0.1206$
$S = 1.005$
3937 reflections
216 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0407P)^2 + 0.322P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.203$ (for H11)
$\Delta\rho_{max} = 0.249$ e Å^{-3}
$\Delta\rho_{min} = -0.210$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for HD1*

Cl1—C8	1.738 (3)	C13—C14	1.506 (3)
Cl2—C12	1.733 (2)	C14—O1	1.233 (3)
N1—C7	1.390 (3)	C14—O2	1.289 (3)
N1—C1	1.411 (3)	O2—H11	1.07 (4)
C2—C13	1.502 (4)		
C7—N1—C1	122.1 (2)	O1—C14—O2	123.7 (2)
C7—N1—H1	115.0 (18)	O1—C14—C13	121.1 (2)
C1—N1—H1	113.8 (19)	O2—C14—C13	115.2 (2)
C1—N1—C7—C12	−62.6 (3)	C2—C13—C14—O2	96.3 (3)
C2—C13—C14—O1	−82.0 (3)		

Table 2. *Hydrogen-bonding geometry (Å, °) for HD1*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.76 (2)	2.65 (2)	2.994 (2)	110 (2)
N1—H1···O1	0.76 (2)	2.37 (2)	3.033 (3)	146 (2)
O2—H11···O1^{i}	1.07 (3)	1.56 (4)	2.629 (3)	177 (3)

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

Compound HD2

Crystal data

$C_{14}H_{11}Cl_2NO_2$
$M_r = 296.14$
Monoclinic
$C2/c$
$a = 20.226\ (4)$ Å
$b = 6.971\ (3)$ Å
$c = 20.061\ (4)$ Å
$\beta = 109.64\ (2)°$
$V = 2664\ (1)$ Å^3
$Z = 8$
$D_x = 1.477$ Mg m^{-3}
$D_m = 1.48$ Mg m^{-3}
D_m measured by flotation in a 1-bromo-3-chloropropane/*p*-xylene mixture

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 7–17°$
$\mu = 0.483$ mm^{-1}
$T = 293\ (2)$ K
Prismatic
0.40 × 0.23 × 0.15 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from ω scans
Absorption correction: none
4383 measured reflections
2589 independent reflections
1743 reflections with $I > 2\sigma(I)$

$R_{int} = 0.024$
$\theta_{max} = 31.54°$
$h = -29 \rightarrow 28$
$k = -9 \rightarrow 9$
$l = -14 \rightarrow 23$
3 standard reflections
frequency: 160 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0374$
$wR(F^2) = 0.1126$
$S = 1.057$
2582 reflections
217 parameters
All H atoms refined

$\Delta\rho_{max} = 0.247$ e Å^{-3}
$\Delta\rho_{min} = -0.249$ e Å^{-3}
Extinction correction: *SHELXL93* (Sheldrick, 1993)
Extinction coefficient: 0.0063 (6)

$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.3396P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.018$

Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for HD2*

Cl1—C8	1.736 (2)	C2—C13	1.507 (4)
Cl2—C12	1.724 (2)	C14—O1	1.216 (2)
N1—C7	1.399 (2)	C14—O2	1.304 (2)
N1—C1	1.415 (3)	O2—H11	0.87 (3)
C7—N1—C1	123.1 (2)	O1—C14—C13	122.4 (2)
C7—N1—H1	110.6 (17)	O2—C14—C13	114.2 (2)
C1—N1—H1	117.8 (18)	C14—O2—H11	109 (2)
O1—C14—O2	123.3 (2)		
C2—C13—C14—O1	−68.3 (3)	C2—C13—C14—O2	109.4 (2)

Table 4. *Hydrogen-bonding geometry (Å, °) for HD2*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···Cl1	0.75 (2)	2.59 (2)	2.987 (2)	115 (2)
N1—H1···O1	0.75 (2)	2.31 (2)	2.946 (3)	143 (2)
O2—H11···O1^{i}	0.87 (3)	1.77 (3)	2.646 (2)	178 (3)

Symmetry code: (i) $\frac{1}{2} - x, -\frac{1}{2} - y, -z$.

For both polymorphs, no absorption correction was applied. All the H atoms were experimentally located and their coordinates and displacement coefficients were isotropically refined.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*93.

The authors thank Servizio Italiano di Diffusione Dati Cristallografici del CNR (Parma) for access to the Cambridge Data Files.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). **C53**, 797–799

N-(2,3,5,6-Tetrachloropyrid-4-yl)cinnamide

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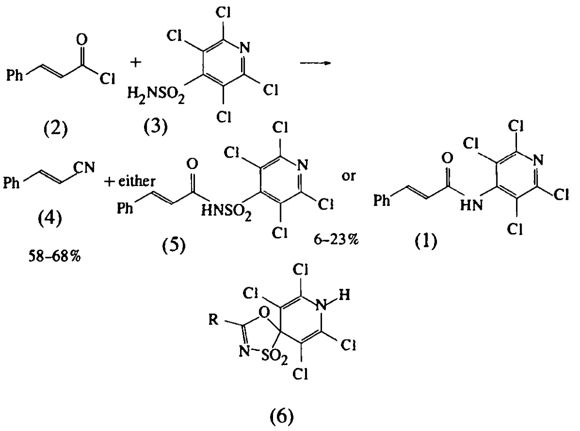
(*Received 24 February 1997; accepted 14 March 1997*)

Abstract

The title compound, $C_{14}H_8Cl_4N_2O$, is an unexpected side product of a reaction to convert an acid chloride into a nitrile, the nature of which indicates the probable mechanism of the major reaction. In the crystal structure, a conjugated and approximately planar cinnamide framework is attached to an almost perpendicular tetrachloro-substituted pyridyl ring, severe steric interactions overcoming the enhanced delocalization which would occur with coplanarity.

Comment

During an investigation into the scope of the reaction for the direct conversion of a carboxylic acid into a nitrile under mild conditions (Tucker & Thomas, 1996), cinnamoyl chloride, (2), was treated with 4-sulfonamido-2,3,5,6-tetrachloropyridine, (3) (Iddon, Mack, Suschitzky, Taylor & Wakefield, 1980) in the presence of triethylamine and a catalytic amount of 4-dimethylaminopyridine. Two products were isolated, the desired 3-phenylpropenenitrile, (4) (in 58% yield), and an unknown crystalline substance to which we initially assigned the structure (5). However, X-ray structure analysis established that the compound was in fact the simple amide (1) (in 20% yield), in which loss of SO_2 from the presumed intermediate (5) had occurred (Fig. 1).



(6)