

$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2 + 0.3396P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.018$

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

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

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Table 3. Selected geometric parameters (\AA , $^\circ$) for HD2

C11—C8	1.736 (2)	C2—C13	1.507 (4)
C12—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 (\AA , $^\circ$) for HD2

D—H...A	D—H	H...A	D...A	D—H...A
N1—H1...C11	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: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL93*.

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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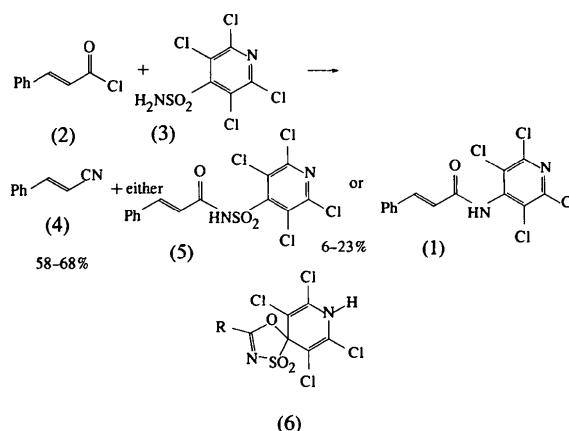
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Abstract

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).



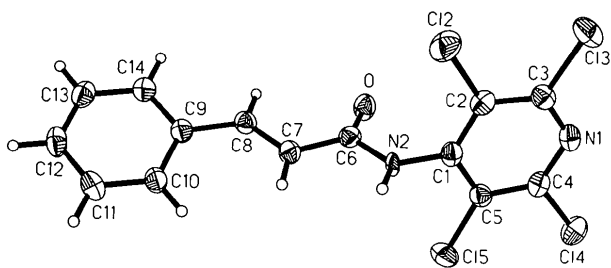


Fig. 1. The molecular structure of the title compound with atom labels and 50% probability ellipsoids for non-H atoms.

We believe that this unusually facile loss of SO₂ provides some insight into the mechanism of the intended conversion of the acid chloride into the nitrile. Both products, (4) and (1), can arise from decomposition of a spirocyclic intermediate (6), formed by addition of the amide O atom to the 4-position of the pyridine ring.

Bond lengths and angles within the molecule of (1) are normal for a conjugated system. The central section of the molecule (atoms N2, O, C6, C7, C8, C9) is essentially planar (r.m.s. deviation 0.045 Å). It is inclined at only 21.1(3)° to the phenyl ring, consistent with a high degree of conjugation, but at 81.2(3)° to the pyridyl ring, which can not adopt coplanarity because of major steric hindrance from the chloro substituents, the carbonyl group and the amide H atom. Less deviation from planarity has been seen in other aromatic substituted cinnamides. Corresponding dihedral angles are 20.2 and 38.9° for cinanserin hydrochloride (Peeters, Blaton & De Ranter, 1986). For the four independent molecules of a 4,6-dimethylpyridin-2-yl derivative, they are 11.0 and 19.5, 12.2 and 10.3, 7.5 and 11.5, and 12.9 and 11.2° (Rodier, Robert-Piessard & Le Baut, 1990). Both these compounds have much less sterically demanding substituents and so can approach planarity.

Experimental

trans-3-Phenylpropenoyl chloride (4.9 mg, 2.46 mmol) in dry dichloromethane (15 ml) was added to a dry flask containing 4-dimethylaminopyridine (15 mg, 0.123 mmol) and 2,3,5,6-tetrachloropyridine-4-sulfonamide (660 mg, 2.23 mmol; Iddon, Mack, Suschitzky, Taylor & Wakefield, 1980) under nitrogen. Dry triethylamine (0.38 ml, 2.7 mmol) was then added and the reactants stirred at room temperature for 60 min. Silica gel (4 g) was added to the solution and the solvent removed under reduced pressure. The silica was transferred to the top of a pre-packed flash chromatography column and the product eluted using petroleum ether–diethyl ether (6:1). The title compound (1) was isolated as a white crystalline solid (m.p. 422–424 K; yield 20%), together with 3-phenylpropenenitrile, (4) (yield 58%). ¹H NMR for (1) (200 MHz, CDCl₃ solution): δ_H 6.7 (1H, *d*, 16 Hz), 7.46 (3H, *m*), 7.62 (2H, *m*), 7.99 (1H, *d*, 16 Hz).

Crystal data

C₁₄H₈Cl₄N₂O
M_r = 362.02
 Monoclinic
*P*2₁/*c*
a = 11.437 (2) Å
b = 7.5790 (10) Å
c = 17.335 (2) Å
 β = 95.09 (3)°
V = 1496.7 (4) Å³
Z = 4
D_x = 1.607 Mg m⁻³
D_m not measured

Mo K α radiation

λ = 0.71073 Å
 Cell parameters from 30 reflections
 θ = 10.94–12.50°
 μ = 0.788 mm⁻¹
T = 160 (2) K
 Block
 0.50 × 0.27 × 0.16 mm
 Colourless

Data collection

Stoe–Siemens diffractometer with Cryostream cooler (Cosier & Glazer, 1986)
 ω/θ scans with on-line profile fitting (Clegg, 1981)
 Absorption correction: none
 3740 measured reflections
 2633 independent reflections

2245 reflections with $I > 2\sigma(I)$
 R_{int} = 0.1090
 θ_{max} = 25°
 h = -13 → 13
 k = -8 → 9
 l = -20 → 20
 4 standard reflections
 frequency: 60 min
 intensity decay: none

Refinement

Refinement on F^2
 $R(F)$ = 0.0464
 $wR(F^2)$ = 0.1267
 S = 1.061
 2633 reflections
 190 parameters
 H atoms riding (see below)
 $w = 1/[\sigma^2(F_o^2) + (0.0549P)^2 + 1.8273P]$
 where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.001
 $\Delta\rho_{max}$ = 0.562 e Å⁻³
 $\Delta\rho_{min}$ = -0.743 e Å⁻³
 Extinction correction: none
 Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O—C6	1.196 (3)	C6—C7	1.463 (4)
N2—C6	1.387 (3)	C7—C8	1.334 (4)
C1—N2—C6	116.9 (2)	N2—C6—C7	110.0 (2)
O—C6—N2	120.9 (2)	C8—C7—C6	119.1 (2)
O—C6—C7	129.1 (3)	C7—C8—C9	127.2 (2)

H atoms were placed geometrically and refined with a riding model and with U_{iso} constrained to be 1.2 times U_{eq} of the carrier atom. The data set consisted of a complete unique set of data together with a partial set of Friedel opposites; the index limits given do not indicate a complete sphere of data. The effects of ignoring absorption are shown to be negligible by refinement from a set of data to which corrections have been applied by an empirical method based on ΔF : the value of R is reduced marginally by 0.003 and all refined parameters show no significant change.

Data collection: *DIF4* (Stoe & Cie, 1988). Cell refinement: *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL*. Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL* and local programs.

The authors thank EPSRC and Zeneca Pharmaceuticals for financial support.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: AB1474). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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10H⁺-2,3-Benzo-1,4-dioxa-7,10,13-triazacyclopentadec-2-ene-6,14-dione Picrate Hydrate (1/1/1)

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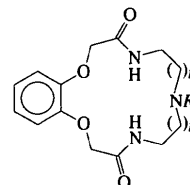
Abstract

The title compound, C₁₄H₂₀N₃O₄·C₆H₂N₃O₇·H₂O, contains a 15-membered macrocycle which has two ether O atoms, two pairs of amide N and O atoms, and an amine N atom as potential donor atoms. The macrocycle has undergone protonation at the amine N atom. The picrate ion interacts through its phenolic O atom

with the NH₂ group *via* an N—H···O hydrogen bond. The water molecule is linked in an endocyclic manner to the macrocyclic ring through both the amide groups by an O···H—N hydrogen bond. The ether O atoms do not participate in any hydrogen-bonding interactions. The water molecule is also intermolecularly linked to one symmetry-related nitro group O atom of the picrate and to one amide O atom.

Comment

Host–guest chemistry is primarily based on the complementarity of the sites of the host with those of the guest. A small change in structure can alter this complementarity (Cram, 1986, 1988) and thus the binding properties of the host. In diamide–diether–amine macrocycles (1a)–(1c), the cavities possess three electron-rich centres (two O atoms and one NH amine atom) and two electron-deficient centres (two NH amide atoms). These macrocycles can therefore interact with electron-rich molecules such as water or alcohols through their amide N atoms and with cations through the ether O atoms and the amine. The previously reported extraction results (Kumar, Singh & Singh, 1992) show a much higher extraction of Pb²⁺ by (1a) and (1b) than is seen for (1c). The X-ray results show that in (1c), water enters the cavity, whereas in (1b), it remains in the lattice (Hundal, Hundal, Kumar, Singh & Sanz-Aparicio, 1995; Hundal *et al.*, 1996). Based on these results, we envisaged that the conversion of (1a) and (1b) into their ammonium salts would render the cavities more electron-deficient and would thus facilitate the encapsulation of small electron-rich molecules like water and simple alcohols.



- (1a) $n = 1$; $R = H$
 (1b) $n = 2$; $R = H$
 (1c) $n = 2$; $R = CH_2CH_2CN$

We present here the results of a structure determination of (1a) picrate hydrate, where a water O atom forms hydrogen bonds with two amide NH units in the cavity of (1a) and water H atoms remain hydrogen bonded with amide O atoms and the *p*-nitro unit of picrate from two different neighbouring molecules. Extensive hydrogen bonding between the ammonium unit of the macrocycle and the picrate anion is also observed. All the bond distances and angles are as expected (Hundal *et al.*, 1996). The structure solution reveals that the picric acid loses its proton to form the picrate anion. The proton