Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

4-Chlorobenzoic acid *N*,*N*-dimethylformamide solvate

Xuelian Xu,[a] Alan R. Kennedy,[b]* Alastair J. Florence[a] and Norman Shankland[a]

[a]Department of Pharmaceutical Sciences, University of Strathclyde, 27 Taylor Street, Glasgow G4 0NR, Scotland, and [b]Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

Correspondence e-mail:
a.r.kennedy@strath.ac.uk

Key indicators

Single-crystal X-ray study
T = 123 K
Mean σ(C–C) = 0.002 Å
R factor = 0.035
wR factor = 0.086
Data-to-parameter ratio = 17.0

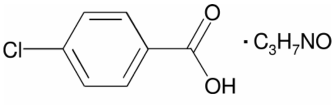
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 17 September 2004
Accepted 30 September 2004
Online 9 October 2004

In the title compound, $C_7H_5ClO_2.C_3H_7NO$, the carboxylic acid group of 4-chlorobenzoic acid is hydrogen bonded to a molecule of *N*,*N*-dimethylformamide *via* an $R_2^2(7)$ O—H···O/C—H···O motif. This motif takes precedence over the $R_2^2(8)$ O—H···O dimer arrangement observed in 4-chlorobenzoic acid itself.

Comment

4-Chlorobenzoic acid (CBA) crystallizes as hydrogen-bonded $R_2^2(8)$ O—H···O dimers and dynamic proton transfer within the hydrogen bonds mediates the interconversion of two inequivalent dimeric forms (Horsewill *et al.*, 2003; Wilson *et al.*, 2004).



(I)

The title compound, (I), was crystallized to determine whether the $R_2^2(8)$ motif, and the proton-transfer process, is preserved in the solvate (Fig. 1). Significant deviations from idealized aromatic geometry in the CBA molecule of (I) include a marked widening of the internal ring angle at C4 [122.26 (12)°] and a concomitant narrowing of the angles *ortho* to this at C3 [118.25 (12)°] and C5 [118.81 (13)°]. Utilizing the angular substituent parameters for Cl and COOH (Domenicano, 1992), the corresponding predicted internal ring angles of 122.1 (C4) and 118.7° (C3 and C5) are in good agreement with the observed values. Thus, it may be concluded that the distortions from ideal sp^2 ring geometry are in line with expectations based on Domenicano's assessment of structural substituent effects in benzene derivatives. The $R_2^2(8)$ motif in CBA [Fig. 2, top, determined from single-crystal neutron diffraction data at 100 K (Wilson *et al.*, 2004)] is not preserved in (I). Instead, one CBA molecule is replaced by one molecule of *N*,*N*-dimethylformamide (DMF), forming an $R_2{}^2(7)$ O—H···O/C—H···O motif (Fig. 2, bottom), eliminating the possibility of a concerted two-proton transfer process. This interaction with DMF is not unexpected, as the $R_2^2(7)$ motif has been observed to recur with a reasonable frequency in the DMF solvates of carboxylic acids (Dale & Elsegood, 2004).

Experimental

A single-crystal sample of the title compound was recrystallized from DMF solution by slow evaporation at room temperature.

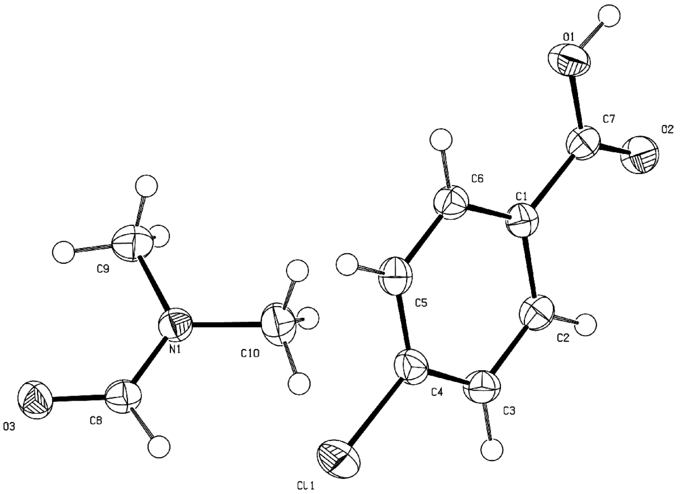


Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids.

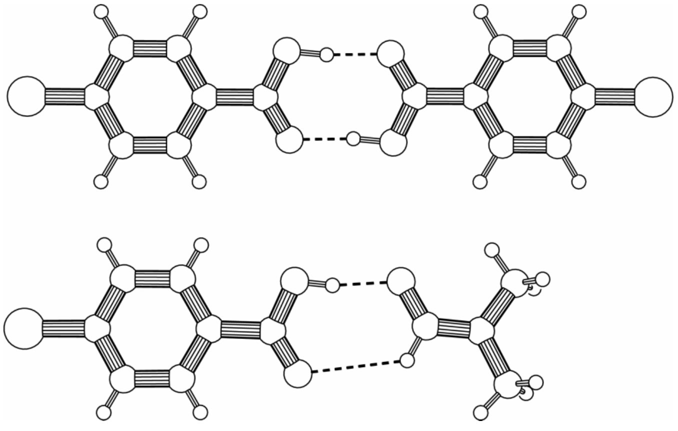


Figure 2
Top: the $R_2^2(8)$ motif in CBA, with O···O = 2.588 (3) Å, O—H = 0.997 (6) Å and H···O = 1.595 (6) Å. Bottom: the $R_2^2(7)$ motif in (I), with O···O = 2.5752 (14) Å, O—H = 0.92 (2) Å, (O)H···O = 1.66 (2) Å and (C—)H···O = 2.716 (14) Å.

Crystal data

$C_7H_5ClO_2 \cdot C_3H_7NO$
$M_r = 229.66$
Monoclinic, $P2_1/c$
$a = 6.1269$ (2) Å
$b = 14.6159$ (5) Å
$c = 12.6541$ (4) Å
$\beta = 103.228$ (2)°
$V = 1103.11$ (6) Å^3
$Z = 4$
$D_x = 1.383$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2512 reflections
$\theta = 1.0$–27.5°
$\mu = 0.33$ mm^{-1}
$T = 123$ (2) K
Cut fragment, colourless
0.50 × 0.45 × 0.40 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: none
10331 measured reflections
2488 independent reflections
2049 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.5°$
$h = -7 \rightarrow 7$
$k = -18 \rightarrow 18$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.086$
$S = 1.02$
2488 reflections
146 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0339P)^2 + 0.445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.31$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.3257 (16)	O3—C8	1.2400 (16)
O2—C7	1.2149 (16)		
C6—C1—C2	119.67 (12)	C5—C6—C1	120.25 (12)
C3—C2—C1	120.76 (12)	O2—C7—O1	123.90 (12)
C2—C3—C4	118.25 (12)	O2—C7—C1	123.13 (12)
C5—C4—C3	122.26 (12)	O1—C7—C1	112.97 (11)
C4—C5—C6	118.81 (13)		

The H atoms involved in hydrogen bonding were located in a difference map and refined isotropically, but all other H atoms were constrained to idealized geometry with a riding model: for CH_3, $U_{\rm iso}(H) = 1.5U_{\rm eq}(C)$ and C—H = 0.98 Å; for CH, $U_{\rm iso}(H) = 1.2U_{\rm eq}(C)$ and C—H = 0.95 Å.

Data collection: *DENZO* (Hooft, 1988) and *COLLECT* (Otwinowski & Minor, 1997); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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