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A redetermination of 4-chloro-3-nitrobenzoic acid

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In the title compound, $C_7H_4ClNO_4$, the molecules form centrosymmetric dimers through O—H$\cdots$O hydrogen bonds. The dimers are connected by C—H$\cdots$O hydrogen bonds to form molecular tapes. Disorder of the H atom in the O—H$\cdots$O hydrogen bond is suggested.

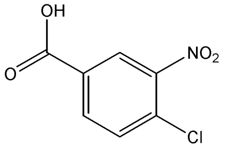
Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ(C–C) = 0.002 Å
R factor = 0.033
wR factor = 0.087
Data-to-parameter ratio = 13.4

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

Comment

The structure determination of the title compound, (I), was originally undertaken by Ferguson & Sim (1959, 1962), using oscillation and Weissenberg photographs, in a series of studies of molecular overcrowding. We have redetermined the crystal structure using diffractometer data, in order to analyze hydrogen-bonding patterns and molecular packing in the crystal structure and to compare the molecular structure with that in the gas phase calculated by *ab initio* molecular-orbital calculation.



(I)

In the crystal structure, two molecules, related by an inversion center, form a dimeric unit *via* strong O—H$\cdots$O hydrogen bonds [O2—H4 = 1.04 (4) Å, H4$\cdots$O1^{i} = 1.60 (4) Å, O2$\cdots$O1^{i} = 2.624 (2) Å and O2—H4$\cdots$O1^{i} = 169 (4)°; symmetry code: (i) $1 - x$, $-1 - y$, $1 - z$; Fig. 1]. Neighboring hydrogen-bonded dimers, related by translation along the a axis, are connected by C—H$\cdots$O hydrogen bonds [C5—H2 = 0.95 (2) Å, H2$\cdots$O2^{ii} = 2.54 (2) Å, C5$\cdots$O2^{ii} = 3.406 (3) Å and C5—H2$\cdots$O2^{ii} = 150.8 (18)°; symmetry code: (ii) $-1 + x$, y, z], forming molecular tapes running along the a axis (Fig. 2). The tapes are stacked in columns along the b axis to form molecular layers extending parallel to the ab plane (Fig. 3).

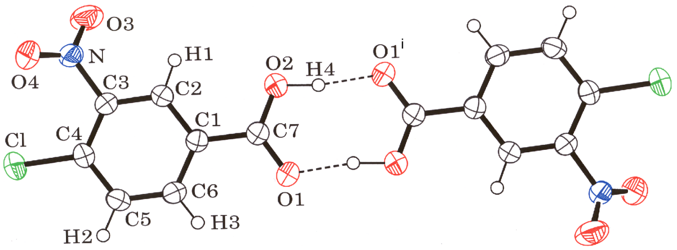


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of a hydrogen-bonded dimer of (I), with the atom-labeling scheme. Displacement ellipsoids of non-H atoms are drawn at the 50% probability level. O—H$\cdots$O hydrogen bonds are indicated by dashed lines. [Symmetry code: (i) $1 - x$, $-1 - y$, $1 - z$.]

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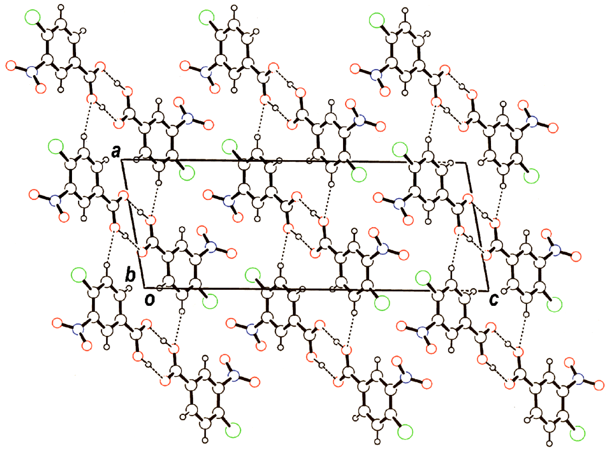

Figure 2
Packing diagram of hydrogen-bonded dimers, viewed along the *b* axis. O—H···O and C—H···O hydrogen bonds are indicated by dashed and dotted lines, respectively

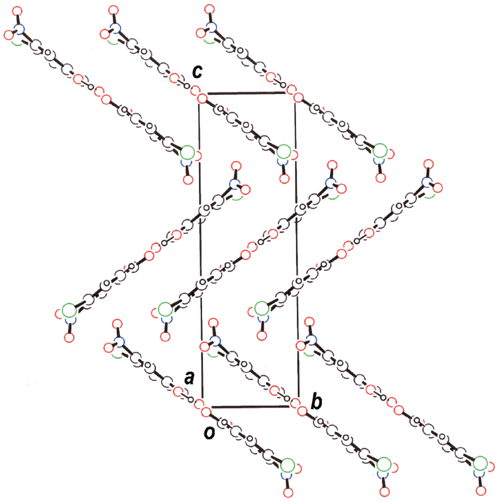

Figure 3
Packing diagram of (I), showing molecular layers extending parallel to the *ab* plane.

The angle between the planes of the benzene ring and the carboxyl group is 7.23 (10)°, and that between the benzene ring and the nitro group is 45.50 (10)°. The H atom of the carboxyl group is located at the O2 site, with a large displacement parameter [$U_{\rm iso}$ = 0.163 (17) Å^2]. This large value can be attributed to the positive effective charge of the acid H atom (Tonogaki *et al.*, 1993) and/or disorder of the H atom in the hydrogen bond. Disorder of the H atom is also suggested by the fact that the C—O bond lengths in the carboxyl group are almost the same [C7—O1 = 1.252 (2) Å and C7—O2 = 1.274 (2) Å], as mentioned below.

The molecular structure in the gas phase was optimized by *ab initio* molecular-orbital calculations at the MP2/6-311G(*d*,*p*) level, using the computer program *GAUSSIAN*98 (Frisch *et al.*, 1998; Møller & Plesset, 1934). The molecule in which the H atom is located at the O2 site was shown to be more stable by 0.65 kJ mol^{-1} in total energy than the molecule in which the H atom is located at the O1 site. This result is consistent with the present crystallographic result. The calculated angle between the planes of the benzene ring and the carboxyl group is 0.64°, and that between the benzene ring and the nitro group is 51.78°. The bond lengths [Cl—C4 = 1.722 Å, N—O3 = 1.230 Å, N—O4 = 1.229 Å, N—C3 = 1.468 Å, C1—C2 = 1.397 Å, C1—C6 = 1.401 Å, C1—C7 = 1.493 Å, C2—C3 = 1.392 Å, C3—C4 = 1.400 Å, C4—C5 = 1.401 Å and C5—C6 = 1.392 Å] are comparable to those given in Table 1, but the calculated C—O bond lengths [C7—O1 = 1.210 Å and C7—O2 = 1.351 Å] in the carboxyl group are apparently shorter and longer, respectively, than the observed bond lengths. This suggests that the H atom involved in the O—H···O hydrogen bond is disordered in an asymmetric double-well potential.

Experimental

Crystals of (I) were obtained from a benzene solution.

Crystal data

$C_7H_4ClNO_4$
M_r = 201.57
Monoclinic, $P2_1/c$
a = 7.404 (3) Å
b = 5.6695 (9) Å
c = 19.144 (3) Å
β = 100.42 (2)°
V = 790.4 (4) Å^3
Z = 4

D_x = 1.694 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 11.8–12.4°
μ = 0.46 mm^{-1}
T = 297 K
Prism, colorless
0.50 × 0.45 × 0.20 mm

Data collection

Rigaku AFC-5*R* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\rm min}$ = 0.839, $T_{\rm max}$ = 0.914
2234 measured reflections
1815 independent reflections
1458 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.011
$\theta_{\rm max}$ = 27.5°
$h = -1 \rightarrow 9$
$k = 0 \rightarrow 7$
$l = -24 \rightarrow 24$
3 standard reflections every 97 reflections intensity decay: 3.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.087
S = 1.06
1815 reflections
135 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0175P)^2 + 0.37P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max}$ = 0.001
$\Delta\rho_{\rm max}$ = 0.27 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.19 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.022 (2)

Table 1
Selected geometric parameters (Å, °).

Cl—C4	1.7215 (18)	C2—C3	1.377 (2)
C7—O1	1.252 (2)	C3—C4	1.391 (2)
C7—O2	1.274 (2)	C4—C5	1.382 (3)
N—O3	1.222 (2)	C5—C6	1.378 (3)
N—O4	1.219 (2)	C2—H1	0.93 (2)
N—C3	1.470 (2)	C5—H2	0.95 (2)
C1—C2	1.390 (2)	C6—H3	0.93 (2)
C1—C6	1.392 (3)	O2—H4	1.04 (4)
C1—C7	1.482 (2)		
O1—C7—O2	123.54 (17)	C2—C3—N	117.19 (15)
O4—N—O3	124.85 (16)	C3—C4—Cl	122.29 (14)
C2—C1—C7	120.37 (16)		

H atoms were found in a difference Fourier map and refined isotropically [C—H = 0.93 (2)–0.95 (2) Å and O—H = 1.04 (4) Å].

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1990); data reduction: *TEXSAN* (Molecular Structure Corporation, 1997–1999); structure solution: *SIR*92 (Altomare *et al.*, 1994); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997); preparation of material for publication: *TEXSAN*.

X-ray measurements were made at the X-ray Laboratory of Okayama University.

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