Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

A redetermination of 2-nitrobenzoic acid

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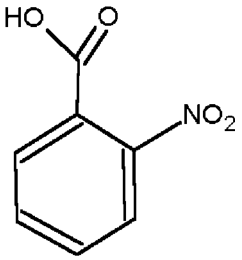
Received 24 March 2009; accepted 30 March 2009

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.077; wR factor = 0.148; data-to-parameter ratio = 16.6.

The crystal structure of the title compound, $C_7H_5NO_4$, was first reported by Kurahashi, Fukuyo & Shimada [(1967). *Bull. Chem. Soc. Jpn*, **40**, 1296]. It has been re-examined, improving the precision of the derived geometric parameters. The asymmetric unit comprises a non-planar independent molecule, as the nitro and the carboxy substituents force each other to be twisted away from the plane of the aromatic ring by 54.9 (2) and 24.0 (2)°, respectively. The molecules form a conventional dimeric unit *via* centrosymmetric intermolecular hydrogen bonds.

Related literature

For the previous structure determination, see: Kurahashi *et al.* (1967); Sakore *et al.* (1967); Tavale & Pant (1973). For the effect of nitro and carboxy substitution on the geometry of polysubstituted benzene rings, see: Colapietro *et al.* (1984); Domenicano *et al.* (1989). For the formation of hydrogen-bonded dimers in monocarboylic acids, see:Leiserowitz (1976). For computation of ring patterns formed by hydrogen bonds in crystal structures, see: Etter *et al.* (1990); Bernstein *et al.* (1995); Motherwell *et al.* (1999).



Experimental

Crystal data

$C_7H_5NO_4$
M_r = 167.12
Triclinic, $P\bar{1}$
a = 5.0147 (15) Å
b = 7.527 (2) Å
c = 10.620 (2) Å
α = 69.41 (2)°
β = 86.07 (2)°
γ = 71.01 (3)°
V = 354.35 (18) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 298 K
0.15 × 0.15 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min}$ = 0.879, $T_{\max}$ = 0.980
3862 measured reflections
1872 independent reflections
1087 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.077
$wR(F^2)$ = 0.148
S = 1.07
1872 reflections
113 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.26 e Å^{-3}
$\Delta\rho_{\min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1$^{\rm i}$	0.90 (3)	1.77 (4)	2.660 (3)	173 (3)

Symmetry code: (i) $-x+2, -y+1, -z+1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

I thank MIUR (Rome) for 2006 financial support of the project 'X-ray diffractometry and spectrometry'.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: KP2213).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Colapietro, M., Domenicano, A., Marciante, C. & Portalone, G. (1984). *Acta Cryst.* A**40**, C98–C99.
Domenicano, A., Schultz, Gy., Hargittai, I., Colapietro, M., Portalone, G., George, P. & Bock, C. W. (1989). *Struct. Chem.* **1**, 107–122.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kurahashi, M., Fukuyo, M. & Shimada, A. (1967). *Bull. Chem. Soc. Jpn*, 40, 1296
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (1999). *Acta Cryst.* B**55**, 1044–1056.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Yarnton, England.
Sakore, T. D., Tavale, S. S. & Pant, L. M. (1967). *Acta Cryst.* **22**, 720–725.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tavale, S. S. & Pant, L. M. (1973). *Acta Cryst.* B**29**, 2979–2980.

supporting information

Acta Cryst. (2009). E**65**, o954 [doi:10.1107/S1600536809011830]

A redetermination of 2-nitrobenzoic acid

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S1. Comment

o-Nitrobenzoic acid was determined more than 40 years ago (Kurahashi *et al.*, 1967), but the final refinement was carried only to *R*=0.18. Subsequently, a new X-ray structure determination was reported (Sakore *et al.*, 1967). In this study, 1250 unique reflections were collected at ambient temperature on an equi-inclination Weissenberg camera using Cu Kα radiation. Data were corrected for Lp effects as well as for the effect of spot extension, but not for absorption [μ(Cu Kα)= 135 mm^{-1}]. 694 visually estimated reflections having values significantly above background were used in the isotropic least-squares refinement. The final calculations led to R = 0.142 for 49 refined parameters, as the H atoms were not localized. A further anisotropic refinement of the structure was eventually carried out (Tavale & Pant, 1973). In this calculation, based on the same data set but with the inclusion of H atoms. the *R* factor decreased to 0.104, with a data-to-parameter ratio of 5.6, and average standard deviations of 0.013Å in C—C bond lengths and 0.9° in bond angles.

The asymmetric unit of (I) comprises a non-planar independent molecule, as the nitro and carboxy substituents force each other to be twisted away from the plane of the aromatic ring by 54.9 (2) and 24.0 (2)°, respectively (Fig. 1). The pattern of bond lengths and bond angles is consistent with those reported in previous structural investigations concerning the effect of the nitro and the carboxy groups on the geometry of polysubstituted benzene rings (Colapietro *et al.*, 1984; Domenicano *et al.*, 1989). Analysis of the crystal packing of (I), (Fig. 2), shows that the molecular components form the conventional dimeric units observed in monocarboylic acids (Leiserowitz, 1976). The structure is stabilized by very short [2.660 (3) Å] intermolecular O—H···O interactions of descriptor $R^2_2(8)$ (Etter *et al.*, 1990; Bernstein *et al.*, 1995; Motherwell *et al.*, 1999) (Table 1) between the OH moiety and the carbonyl O atom (O1^{i}) [symmetry code: (i) $-x + 2$, $-y + 1$, $-z + 1$].

S2. Experimental

o-Nitrobenzoic acid (0.1 mmol, Sigma Aldrich at 95% purity) was dissolved in water (5 ml) and gently heated under reflux for 1 h. After cooling the solution to an ambient temperature, crystals suitable for single-crystal X-ray diffraction were grown by slow evaporation of the solvent after few days.

S3. Refinement

All H atoms were found in a difference map and then treated as riding atoms, with C—H = 0.93Å and U_{iso} values equal to $1.2U_{eq}$(C, phenyl). The remaining H atom of the carboxy group was freely refined.

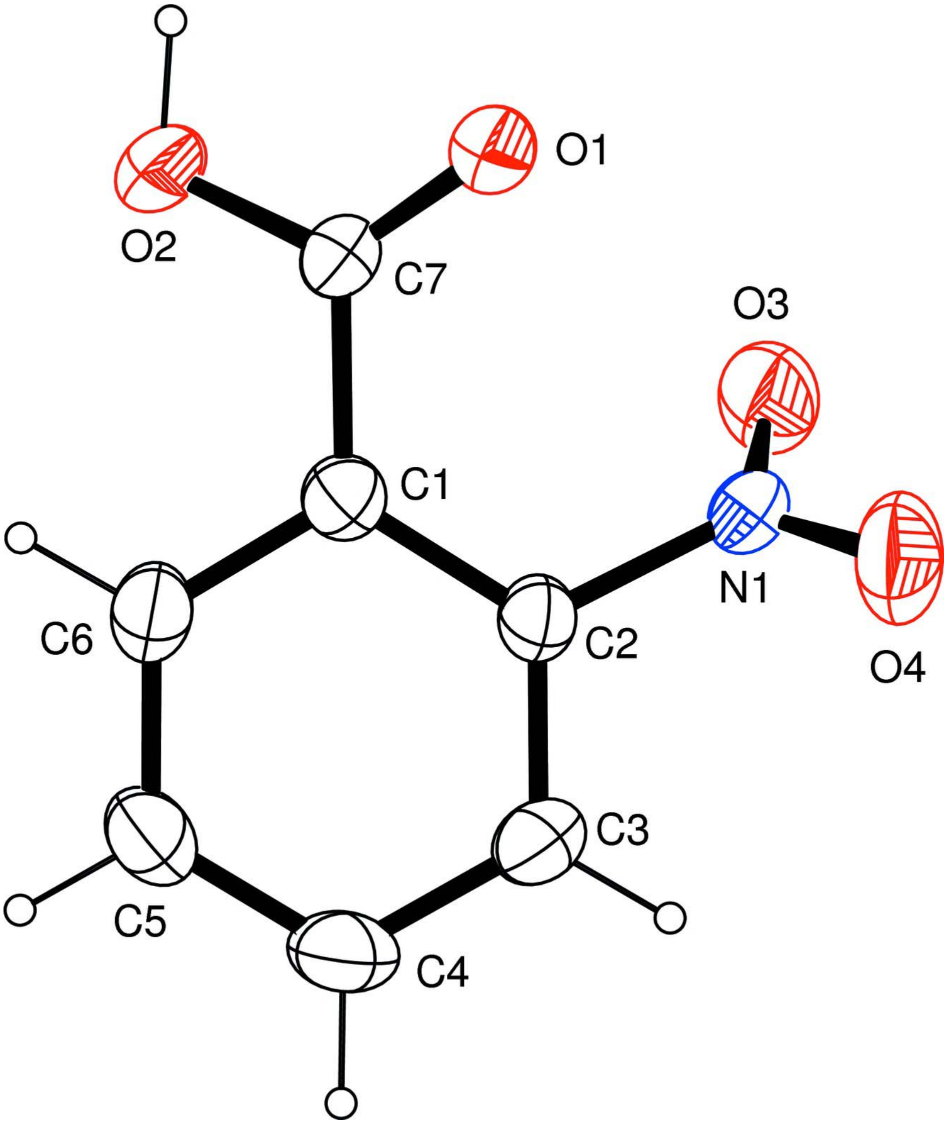

Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacements ellipsoids are at the 50% probability level.

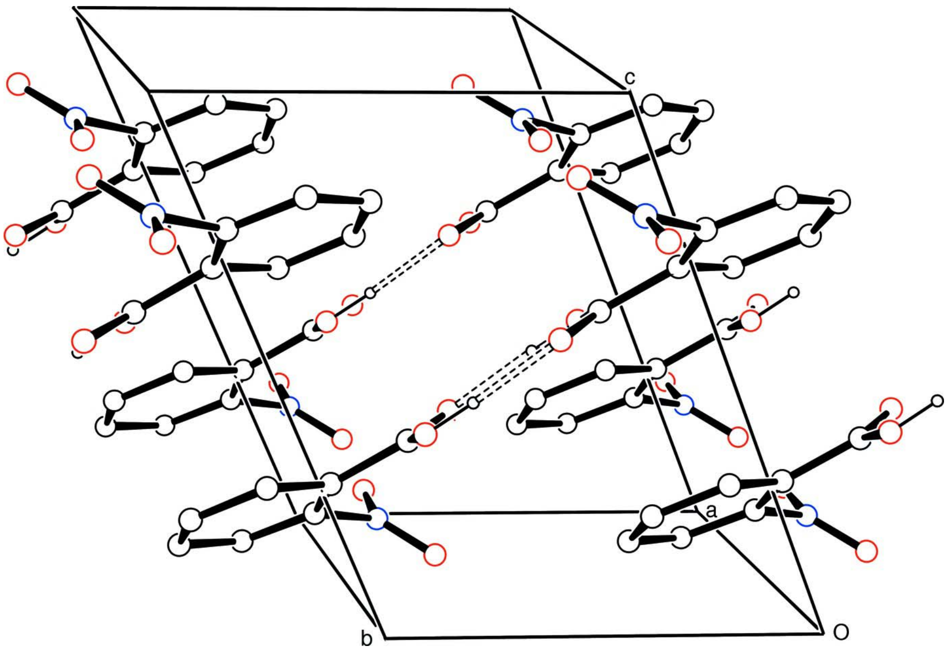

Figure 2

Crystal packing diagram for (I) viewed approximately down a. All atoms are shown as small spheres of arbitrary radii. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonding is indicated by dashed lines.

2-nitrobenzoic acid

Crystal data

$C_7H_5NO_4$
$M_r = 167.12$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 5.0147$ (15) Å
$b = 7.527$ (2) Å
$c = 10.620$ (2) Å
$\alpha = 69.41$ (2)°
$\beta = 86.07$ (2)°
$\gamma = 71.01$ (3)°
$V = 354.35$ (18) Å^3
$Z = 2$
$F(000) = 172$
$D_x = 1.566$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 861 reflections
$\theta = 3.0$–32.5°
$\mu = 0.13$ mm^{-1}
$T = 298$ K
Tablets, colourless
0.15 × 0.15 × 0.10 mm

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0696 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006)
$T_{\min} = 0.879$, $T_{\max} = 0.980$
3862 measured reflections
1872 independent reflections
1087 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.050$
$\theta_{\max} = 29.0$°, $\theta_{\min} = 3.0$°
$h = -6 \rightarrow 6$
$k = -10 \rightarrow 10$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.077$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.148$	$w = 1/[\sigma^2(F_o^2) + (0.0536P)^2 + 0.0451P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1872 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
113 parameters	$\Delta\rho_{min} = -0.20$ e Å^{-3}
0 restraints	
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. Absorption correction: CrysAlis RED, Oxford Diffraction Ltd., Version 1.171.32.29 (release 10-06-2008 CrysAlis171 .NET) (compiled Jun 10 2008,16:49:55) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.8083 (4)	0.3762 (3)	0.6058 (2)	0.0471 (6)
O2	1.2483 (4)	0.2482 (3)	0.5512 (2)	0.0481 (6)
H2	1.221 (7)	0.378 (5)	0.504 (3)	0.068 (11)*
O3	0.7790 (4)	0.2147 (3)	0.8921 (2)	0.0537 (6)
O4	0.4118 (4)	0.1514 (3)	0.8517 (2)	0.0533 (6)
N1	0.6642 (5)	0.1288 (3)	0.8481 (2)	0.0344 (5)
C1	1.0287 (5)	0.0235 (3)	0.6923 (2)	0.0305 (6)
C2	0.8416 (5)	−0.0231 (4)	0.7933 (2)	0.0297 (6)
C3	0.8224 (6)	−0.2123 (4)	0.8508 (3)	0.0381 (7)
H3	0.6904	−0.2375	0.9147	0.046*
C4	1.0025 (6)	−0.3648 (4)	0.8123 (3)	0.0450 (7)
H4	0.9927	−0.4941	0.8503	0.054*
C5	1.1971 (6)	−0.3249 (4)	0.7172 (3)	0.0440 (8)
H5	1.3219	−0.4286	0.6933	0.053*
C6	1.2084 (6)	−0.1327 (4)	0.6572 (3)	0.0393 (7)
H6	1.3386	−0.1080	0.5922	0.047*
C7	1.0188 (5)	0.2327 (4)	0.6144 (3)	0.0334 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0457 (12)	0.0296 (10)	0.0542 (13)	−0.0083 (9)	0.0228 (10)	−0.0080 (9)

O2	0.0461 (13)	0.0350 (12)	0.0543 (13)	−0.0151 (9)	0.0236 (10)	−0.0071 (10)
O3	0.0600 (14)	0.0563 (13)	0.0657 (14)	−0.0290 (11)	0.0177 (11)	−0.0391 (12)
O4	0.0361 (12)	0.0638 (14)	0.0638 (15)	−0.0131 (10)	0.0160 (10)	−0.0321 (12)
N1	0.0411 (14)	0.0319 (12)	0.0275 (12)	−0.0140 (10)	0.0117 (10)	−0.0071 (10)
C1	0.0335 (14)	0.0287 (14)	0.0275 (13)	−0.0088 (11)	0.0023 (11)	−0.0090 (11)
C2	0.0312 (13)	0.0300 (14)	0.0270 (13)	−0.0084 (10)	0.0045 (11)	−0.0106 (11)
C3	0.0486 (17)	0.0355 (15)	0.0323 (15)	−0.0205 (12)	0.0114 (13)	−0.0097 (12)
C4	0.062 (2)	0.0263 (14)	0.0437 (17)	−0.0150 (13)	0.0056 (15)	−0.0079 (13)
C5	0.0530 (18)	0.0312 (15)	0.0436 (17)	−0.0052 (12)	0.0085 (14)	−0.0169 (13)
C6	0.0402 (16)	0.0393 (16)	0.0357 (15)	−0.0105 (12)	0.0132 (13)	−0.0138 (13)
C7	0.0392 (15)	0.0320 (14)	0.0304 (14)	−0.0148 (12)	0.0131 (12)	−0.0116 (11)

Geometric parameters (Å, º)

O1—C7	1.222 (3)	C2—C3	1.372 (3)
O2—C7	1.310 (3)	C3—C4	1.380 (3)
O2—H2	0.90 (3)	C3—H3	0.9300
O3—N1	1.208 (3)	C4—C5	1.381 (4)
O4—N1	1.221 (3)	C4—H4	0.9300
N1—C2	1.474 (3)	C5—C6	1.379 (4)
C1—C6	1.381 (3)	C5—H5	0.9300
C1—C2	1.402 (3)	C6—H6	0.9300
C1—C7	1.485 (3)		

C7—O2—H2	108 (2)	C3—C4—C5	119.8 (2)
O3—N1—O4	124.6 (2)	C3—C4—H4	120.1
O3—N1—C2	118.2 (2)	C5—C4—H4	120.1
O4—N1—C2	117.1 (2)	C6—C5—C4	120.6 (2)
C6—C1—C2	117.2 (2)	C6—C5—H5	119.7
C6—C1—C7	119.9 (2)	C4—C5—H5	119.7
C2—C1—C7	122.7 (2)	C5—C6—C1	120.9 (2)
C3—C2—C1	122.5 (2)	C5—C6—H6	119.6
C3—C2—N1	116.4 (2)	C1—C6—H6	119.6
C1—C2—N1	121.1 (2)	O1—C7—O2	123.4 (2)
C2—C3—C4	118.9 (2)	O1—C7—C1	122.2 (2)
C2—C3—H3	120.6	O2—C7—C1	114.4 (2)
C4—C3—H3	120.6		

C6—C1—C2—C3	−3.7 (4)	C2—C3—C4—C5	−0.1 (4)
C7—C1—C2—C3	169.9 (3)	C3—C4—C5—C6	−1.9 (4)
C6—C1—C2—N1	173.2 (2)	C4—C5—C6—C1	1.1 (4)
C7—C1—C2—N1	−13.3 (4)	C2—C1—C6—C5	1.6 (4)
O3—N1—C2—C3	122.6 (3)	C7—C1—C6—C5	−172.1 (3)
O4—N1—C2—C3	−53.9 (3)	C6—C1—C7—O1	152.9 (3)
O3—N1—C2—C1	−54.5 (3)	C2—C1—C7—O1	−20.5 (4)
O4—N1—C2—C1	129.1 (3)	C6—C1—C7—O2	−23.9 (4)
C1—C2—C3—C4	2.9 (4)	C2—C1—C7—O2	162.7 (2)
N1—C2—C3—C4	−174.1 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O1^{i}	0.90 (3)	1.77 (4)	2.660 (3)	173 (3)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.