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5-Bromo-2-(phenylamino)benzoic acid

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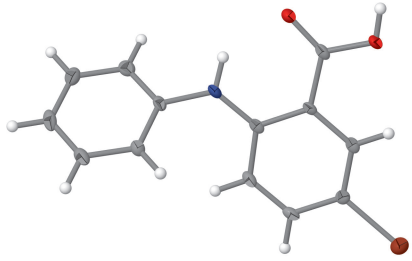
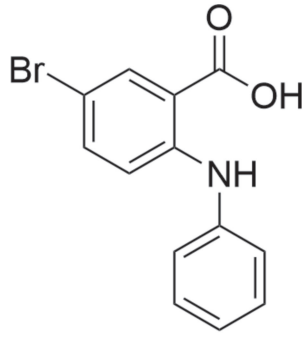
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{13}H_{10}BrNO_2$, was obtained by the reaction of 2,5-dibromobenzoic acid and aniline. The molecule is twisted with a dihedral angle between the aromatic rings of 45.74 (11)° and an intramolecular N—H···O hydrogen bond is seen. In the crystal, pairwise O—H···O hydrogen bonds generate carboxylic acid inversion dimers.

3D view



Chemical scheme



Structure description

Non-steroidal anti-inflammatory drugs are among the most widely used drugs in the world (Enthoven *et al.*, 2017). These have anti-inflammatory, antipyretic and analgesic effects and can be sold as prescription drugs and over-the-counter drugs for the treatment of fever, acute or chronic pain and a variety of inflammatory diseases such as osteoarthritis, rheumatoid arthritis, *etc* (Machado *et al.*, 2021).

As part of our studies in this area, we now describe the synthesis by the Ullman reaction (Wolf *et al.*, 2006) and the crystal structure of the title compound, $C_{13}H_{10}BrNO_2$. As a result of steric repulsion, the C1–C6 and C8–C13 aromatic rings are twisted, subtending a dihedral angle of 45.39 (11)°. An intramolecular N7—H7···O15 hydrogen bond is seen (Fig. 1, Table 1). In the extended structure, the molecules pair up to form carboxylic acid inversion dimers linked by pairs of O16—H16···O15 hydrogen bonds (Fig. 2, Table 1).

Synthesis and crystallization

The title compound was prepared by reacting 2,5-dibromobenzoic acid and aniline in the presence of a catalyst at 403 K (Fig. 3). The product was purified by column chromatography. Single crystals were obtained by slowly evaporating an acetone solution of the title compound.

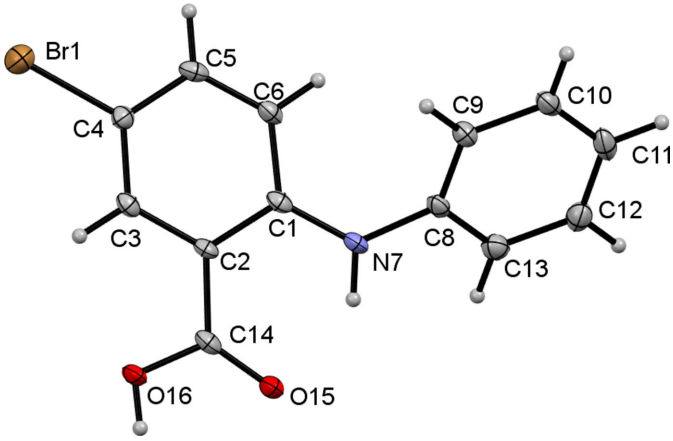


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

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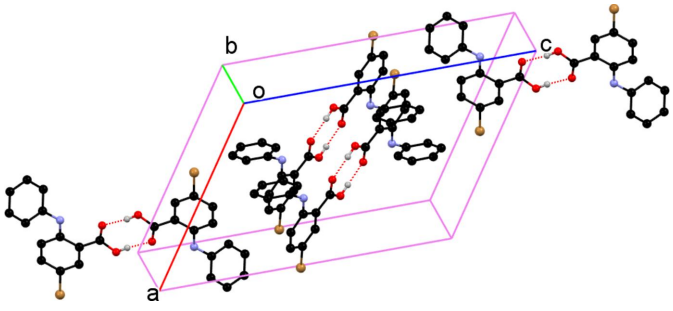

Figure 2
Packing of the molecules in the title compound (for clarity, H atoms not involved in intermolecular hydrogen bonding are omitted).

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

D—H···A	D—H	H···A	D···A	D—H···A
N7—H7···O15	0.88	2.00	2.682 (4)	134
O16—H16···O15^{i}	0.84	1.79	2.629 (4)	174

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

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{13}H_{10}BrNO_2$
M_r	292.13
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	90
a, b, c (Å)	15.2054 (3), 3.8818 (1), 19.8109 (4)
β (°)	107.0391 (10)
V (Å^3)	1118.00 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	3.66
Crystal size (mm)	0.20 × 0.10 × 0.05
Data collection	
Diffractometer	Nonius KappaCCD diffractometer
Absorption correction	Multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min}, T_{max}	0.528, 0.838
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4587, 2550, 2206
R_{int}	0.026
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.130, 1.21
No. of reflections	2550
No. of parameters	155
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.67, −0.81

Computer programs: *COLLECT* (Nonius, 2002), *DENZO-SMN* (Otwinowski & Minor, 1997), *SHELXS97* and *SHELXL97* (Sheldrick, 2015) and *XP* in *SHELXTL* (Sheldrick, 2008).

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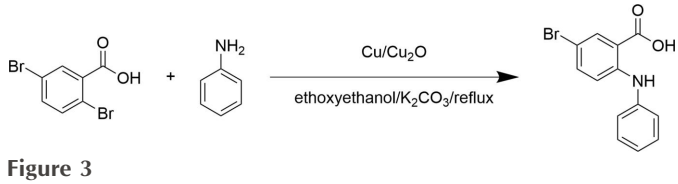

Figure 3
Synthesis of the title compound.

full crystallographic data

IUCrData (2024). **9**, x240198 [https://doi.org/10.1107/S2414314624001986]

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5-Bromo-2-(phenylamino)benzoic acid

Crystal data

$C_{13}H_{10}BrNO_2$
M_r = 292.13
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
a = 15.2054 (3) Å
b = 3.8818 (1) Å
c = 19.8109 (4) Å
β = 107.0391 (10)°
V = 1118.00 (4) Å^3
Z = 4
$F(000)$ = 584
D_x = 1.736 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2931 reflections
θ = 1.0–27.5°
μ = 3.66 mm^{-1}
T = 90 K
Rod, yellow
0.20 × 0.10 × 0.05 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 18 pixels mm^{-1}
ω scans at fixed χ=55°
Absorption correction: multi-scan (Scalepack; Otwinowski & Minor, 1997)
T_{min} = 0.528, T_{max} = 0.838
4587 measured reflections
2550 independent reflections
2206 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 27.5°, θ_{min} = 1.5°
h = −19→19
k = −4→5
l = −25→25

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.130
S = 1.21
2550 reflections
155 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0621P)^2 + 2.3209P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.67 e Å^{-3}
$\Delta\rho_{min}$ = −0.81 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 $F^2 > 2\text{sigma}(F^2)$ 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.
The positions of the H atoms attached to N1 and O1 were obtained from a difference Fourier map. The other H atoms were positioned geometrically with C—H = 0.95 Å and constrained to ride on their parent atoms with $U_{iso}(H) = 1.2U_{eq}(C,N)$ or $1.5U_{eq}(O)$.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.10141 (2)	0.46781 (11)	0.57989 (2)	0.02709 (16)
C1	0.4236 (2)	0.5204 (8)	0.66869 (17)	0.0142 (7)
C2	0.3806 (2)	0.3697 (9)	0.60154 (16)	0.0129 (6)
C3	0.2839 (2)	0.3583 (9)	0.57554 (16)	0.0142 (6)
H3	0.2554	0.2540	0.5311	0.017*
C4	0.2307 (2)	0.4972 (9)	0.61400 (17)	0.0149 (7)
C5	0.2722 (2)	0.6592 (9)	0.67881 (17)	0.0154 (7)
H5	0.2351	0.7620	0.7044	0.018*
C6	0.3662 (2)	0.6696 (9)	0.70531 (16)	0.0155 (7)
H6	0.3933	0.7796	0.7493	0.019*
N7	0.5173 (2)	0.5306 (8)	0.69514 (15)	0.0172 (6)
H7	0.5482	0.4840	0.6650	0.021*
C8	0.5710 (2)	0.6066 (9)	0.76502 (17)	0.0149 (7)
C9	0.5449 (2)	0.4996 (9)	0.82367 (18)	0.0162 (7)
H9	0.4883	0.3826	0.8176	0.019*
C10	0.6029 (3)	0.5664 (9)	0.89132 (18)	0.0192 (7)
H10	0.5851	0.4970	0.9314	0.023*
C11	0.6858 (3)	0.7323 (10)	0.90048 (18)	0.0221 (8)
H11	0.7246	0.7782	0.9467	0.026*
C12	0.7125 (2)	0.8319 (10)	0.84229 (19)	0.0214 (7)
H12	0.7704	0.9403	0.8487	0.026*
C13	0.6547 (2)	0.7736 (10)	0.77441 (18)	0.0195 (7)
H13	0.6723	0.8478	0.7346	0.023*
C14	0.4345 (2)	0.2211 (9)	0.55789 (16)	0.0156 (7)
O15	0.51870 (16)	0.2210 (7)	0.57446 (12)	0.0211 (6)
O16	0.38326 (17)	0.0837 (7)	0.49767 (12)	0.0199 (5)
H16	0.4176	−0.0037	0.4759	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0193 (2)	0.0366 (3)	0.0254 (2)	0.00184 (16)	0.00662 (16)	−0.00424 (16)
C1	0.0205 (16)	0.0130 (16)	0.0102 (14)	−0.0001 (13)	0.0061 (12)	0.0015 (12)
C2	0.0175 (15)	0.0140 (15)	0.0089 (13)	−0.0007 (13)	0.0063 (12)	0.0002 (12)
C3	0.0191 (16)	0.0128 (15)	0.0104 (14)	0.0001 (13)	0.0036 (12)	0.0012 (12)
C4	0.0149 (15)	0.0170 (17)	0.0130 (15)	0.0015 (13)	0.0043 (12)	0.0030 (12)
C5	0.0232 (17)	0.0128 (16)	0.0132 (14)	0.0021 (14)	0.0100 (13)	0.0008 (13)

C6	0.0222 (17)	0.0144 (16)	0.0097 (13)	0.0028 (14)	0.0041 (12)	−0.0003 (12)
N7	0.0181 (14)	0.0250 (17)	0.0095 (12)	−0.0002 (12)	0.0054 (11)	−0.0044 (11)
C8	0.0179 (16)	0.0148 (16)	0.0114 (14)	0.0014 (13)	0.0034 (12)	−0.0037 (13)
C9	0.0180 (16)	0.0171 (17)	0.0130 (15)	−0.0004 (13)	0.0039 (12)	−0.0013 (13)
C10	0.0238 (18)	0.0208 (18)	0.0122 (15)	0.0067 (14)	0.0040 (13)	−0.0006 (13)
C11	0.0246 (18)	0.0205 (19)	0.0153 (15)	0.0074 (15)	−0.0033 (13)	−0.0035 (14)
C12	0.0169 (16)	0.0216 (19)	0.0235 (17)	0.0012 (15)	0.0023 (14)	−0.0037 (15)
C13	0.0209 (17)	0.0201 (18)	0.0180 (16)	0.0027 (14)	0.0066 (13)	−0.0011 (14)
C14	0.0219 (17)	0.0159 (16)	0.0094 (13)	−0.0006 (14)	0.0053 (12)	−0.0002 (12)
O15	0.0161 (12)	0.0342 (15)	0.0135 (11)	−0.0013 (11)	0.0052 (9)	−0.0074 (11)
O16	0.0169 (12)	0.0315 (15)	0.0123 (11)	−0.0035 (11)	0.0058 (9)	−0.0096 (10)

Geometric parameters (Å, º)

Br1—C4	1.885 (3)	C8—C13	1.390 (5)
C1—N7	1.368 (5)	C8—C9	1.397 (5)
C1—C6	1.412 (5)	C9—C10	1.396 (5)
C1—C2	1.424 (4)	C9—H9	0.9500
C2—C3	1.409 (5)	C10—C11	1.379 (6)
C2—C14	1.471 (4)	C10—H10	0.9500
C3—C4	1.374 (5)	C11—C12	1.385 (5)
C3—H3	0.9500	C11—H11	0.9500
C4—C5	1.403 (5)	C12—C13	1.393 (5)
C5—C6	1.371 (5)	C12—H12	0.9500
C5—H5	0.9500	C13—H13	0.9500
C6—H6	0.9500	C14—O15	1.226 (4)
N7—C8	1.417 (4)	C14—O16	1.330 (4)
N7—H7	0.8800	O16—H16	0.8400
N7—C1—C6	121.5 (3)	C13—C8—N7	118.1 (3)
N7—C1—C2	120.7 (3)	C9—C8—N7	121.9 (3)
C6—C1—C2	117.7 (3)	C10—C9—C8	119.3 (3)
C3—C2—C1	119.8 (3)	C10—C9—H9	120.3
C3—C2—C14	118.3 (3)	C8—C9—H9	120.3
C1—C2—C14	121.9 (3)	C11—C10—C9	120.6 (3)
C4—C3—C2	120.4 (3)	C11—C10—H10	119.7
C4—C3—H3	119.8	C9—C10—H10	119.7
C2—C3—H3	119.8	C10—C11—C12	120.0 (3)
C3—C4—C5	120.2 (3)	C10—C11—H11	120.0
C3—C4—Br1	120.0 (3)	C12—C11—H11	120.0
C5—C4—Br1	119.9 (3)	C11—C12—C13	120.1 (4)
C6—C5—C4	120.2 (3)	C11—C12—H12	119.9
C6—C5—H5	119.9	C13—C12—H12	119.9
C4—C5—H5	119.9	C8—C13—C12	119.9 (3)
C5—C6—C1	121.5 (3)	C8—C13—H13	120.0
C5—C6—H6	119.2	C12—C13—H13	120.0
C1—C6—H6	119.2	O15—C14—O16	122.1 (3)
C1—N7—C8	128.2 (3)	O15—C14—C2	124.1 (3)

C1—N7—H7	115.9	O16—C14—C2	113.8 (3)
C8—N7—H7	115.9	C14—O16—H16	109.5
C13—C8—C9	119.9 (3)		
N7—C1—C2—C3	179.3 (3)	C1—N7—C8—C13	−147.3 (4)
C6—C1—C2—C3	−3.1 (5)	C1—N7—C8—C9	36.8 (5)
N7—C1—C2—C14	−0.3 (5)	C13—C8—C9—C10	0.9 (5)
C6—C1—C2—C14	177.3 (3)	N7—C8—C9—C10	176.7 (3)
C1—C2—C3—C4	1.1 (5)	C8—C9—C10—C11	−0.9 (5)
C14—C2—C3—C4	−179.3 (3)	C9—C10—C11—C12	−0.5 (6)
C2—C3—C4—C5	1.6 (5)	C10—C11—C12—C13	1.8 (6)
C2—C3—C4—Br1	−178.1 (3)	C9—C8—C13—C12	0.4 (5)
C3—C4—C5—C6	−2.2 (5)	N7—C8—C13—C12	−175.6 (3)
Br1—C4—C5—C6	177.4 (3)	C11—C12—C13—C8	−1.7 (6)
C4—C5—C6—C1	0.2 (5)	C3—C2—C14—O15	178.8 (3)
N7—C1—C6—C5	−180.0 (3)	C1—C2—C14—O15	−1.6 (6)
C2—C1—C6—C5	2.4 (5)	C3—C2—C14—O16	−1.2 (5)
C6—C1—N7—C8	15.9 (5)	C1—C2—C14—O16	178.4 (3)
C2—C1—N7—C8	−166.6 (3)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N7—H7···O15	0.88	2.00	2.682 (4)	134
O16—H16···O15^{i}	0.84	1.79	2.629 (4)	174

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