

4-Bromoanilinium hydrogen phthalate

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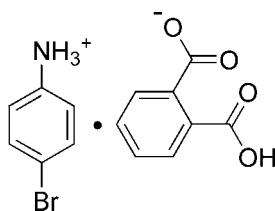
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 Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.011$ Å; R factor = 0.054; wR factor = 0.127; data-to-parameter ratio = 12.7.

In the anion of the title compound, $\text{C}_6\text{H}_7\text{BrN}^+\cdot\text{C}_8\text{H}_5\text{O}_4^-$, the dihedral angles formed by the benzene ring and the mean planes of the $-\text{COOH}$ and $-\text{COO}^-$ groups are 20.6 (3) and 83.2 (3)°, respectively. In the crystal, intermolecular $\text{N}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds connect the cations and anions, forming a two-dimensional network parallel to (001).

Related literature

For applications of phthalimides and N -substituted phthalimides, see: Lima *et al.* (2002). For the crystal structures of 4-chloroanilinium, 2-hydroxyanilinium and 3-hydroxyanilinium hydrogen phthalates, see: Jagan & Sivakumar (2009).



Experimental

Crystal data

$\text{C}_6\text{H}_7\text{BrN}^+\cdot\text{C}_8\text{H}_5\text{O}_4^-$
 $M_r = 338.16$
 Monoclinic, $C2$
 $a = 13.0890$ (14) Å
 $b = 7.6670$ (7) Å
 $c = 14.6900$ (14) Å
 $\beta = 106.671$ (1)°

$V = 1412.2$ (2) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 2.92$ mm⁻¹
 $T = 298$ K
 $0.41 \times 0.37 \times 0.18$ mm

Data collection

Bruker SMART CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 1997)
 $T_{\min} = 0.380$, $T_{\max} = 0.621$

3555 measured reflections
 2364 independent reflections
 1659 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.127$
 $S = 0.94$
 2364 reflections
 186 parameters
 1 restraint

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.82$ e Å⁻³
 $\Delta\rho_{\min} = -0.51$ e Å⁻³
 Absolute structure: Flack (1983), 1027 Friedel pairs
 Flack parameter: 0.012 (16)

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

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{O2}-\text{H2}\cdots\text{O3}^{\text{i}}$ | 0.80 (6) | 1.76 (6) | 2.518 (6) | 158 (7) |
| $\text{N1}-\text{H1C}\cdots\text{O4}$ | 0.89 | 2.37 | 2.962 (7) | 125 |
| $\text{N1}-\text{H1C}\cdots\text{O1}^{\text{ii}}$ | 0.89 | 2.13 | 2.916 (7) | 147 |
| $\text{N1}-\text{H1B}\cdots\text{O4}^{\text{iii}}$ | 0.89 | 1.96 | 2.804 (7) | 159 |
| $\text{N1}-\text{H1A}\cdots\text{O3}^{\text{iv}}$ | 0.89 | 1.96 | 2.828 (6) | 164 |

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + 1$; (ii) $x, y - 1, z$; (iii) $-x + 1, y, -z + 1$; (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH5245).

References

- Bruker (1997). *SADABS*, *SMART* and *SAINT*, Bruker AXS Inc., Madison, Wisconsin, USA.
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supplementary materials

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4-Bromoanilinium hydrogen phthalate

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Comment

Phthalimides and N-substituted phthalimides are an important class of compounds because of their interesting biological activities (Lima *et al.*, 2002). 4-Bromoanilinium hydrogen phthalate is an intermediate in the preparation of N-substituted phthalimides. The crystal structures of 4-chloroanilinium, 2-hydroxyanilinium and 3-hydroxyanilinium hydrogen phthalates have already been reported (Jagan & Sivakumar, 2009). In this paper, the structure of the title compound is reported. The asymmetric unit of the title compound (I) contains one 4-bromoanilinium cation and one hydrogen phthalate anion (Fig. 1). The dihedral angles formed by the benzene ring and the mean planes of the —COOH and —COO⁻ groups are 20.6 (3) and 83.2 (3) °, respectively. In the crystal, intermolecular N—H···O and O—H···O hydrogen bonds connect cations and anions to form a two-dimensional network parallel to (001) (Fig. 2).

Experimental

A mixture of phthalic anhydride (1.52 g, 0.01 mol) and 4-bromoaniline (1.72 g, 0.01 mol) in 20 ml ethanol(95%) solution was refluxed for 0.5 h. The solution was kept at room temperature for 7 d. Natural evaporation gave colourless single crystals of the title compound, suitable for X-ray analysis.

Refinement

H atoms bonded to C and N were initially located in difference maps and then refined in a riding-model approximation with C—H = 0.93 Å and N—H = 0.89 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ or $1.5U_{\text{eq}}(\text{N})$. The H atom bonded to O was refined independently with an isotropic displacement parameter.

Figures

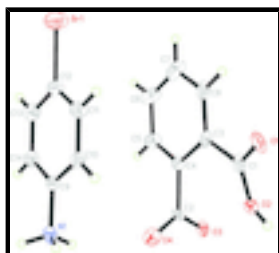


Fig. 1. The asymmetric unit of (I), drawn with 30% probability ellipsoids.

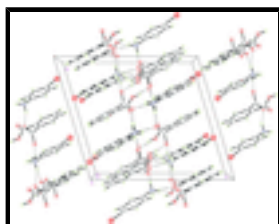


Fig. 2. Part of the crystal structure of the title compound with hydrogen bonds shown as dashed lines.

4-Bromoanilinium 2-carboxybenzoate

Crystal data

$C_6H_7BrN^+ \cdot C_8H_5O_4^-$

$M_r = 338.16$

Monoclinic, C2

Hall symbol: C 2y

$a = 13.0890$ (14) Å

$b = 7.6670$ (7) Å

$c = 14.6900$ (14) Å

$\beta = 106.671$ (1)°

$V = 1412.2$ (2) Å³

$Z = 4$

$F(000) = 680$

$D_x = 1.590$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1173 reflections

$\theta = 2.9$ – 20.8 °

$\mu = 2.92$ mm⁻¹

$T = 298$ K

Block, colorless

$0.41 \times 0.37 \times 0.18$ mm

Data collection

Bruker SMART CCD
diffractometer

Radiation source: fine-focus sealed tube
graphite

φ and ω scans

Absorption correction: multi-scan
(*SADABS*; Bruker, 1997)

$T_{\min} = 0.380$, $T_{\max} = 0.621$

3555 measured reflections

2364 independent reflections

1659 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.045$

$\theta_{\max} = 25.0$ °, $\theta_{\min} = 2.9$ °

$h = -13 \rightarrow 15$

$k = -8 \rightarrow 9$

$l = -17 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.127$

$S = 0.94$

2364 reflections

186 parameters

1 restraint

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H atoms treated by a mixture of independent and
constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0642P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.82$ e Å⁻³

$\Delta\rho_{\min} = -0.51$ e Å⁻³

Absolute structure: Flack (1983), 1027 Friedel pairs

Flack parameter: 0.012 (16)

Special details

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 (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|--------------|-------------|----------------------------------|
| Br1 | 0.16160 (6) | 0.43398 (15) | 0.05674 (5) | 0.0677 (3) |
| N1 | 0.3761 (4) | -0.0249 (6) | 0.4004 (3) | 0.0329 (13) |
| H1A | 0.3407 | -0.1253 | 0.3952 | 0.049* |
| H1B | 0.3731 | 0.0303 | 0.4528 | 0.049* |
| H1C | 0.4438 | -0.0462 | 0.4035 | 0.049* |
| O1 | 0.5651 (4) | 0.7623 (6) | 0.4163 (4) | 0.0553 (16) |
| O2 | 0.6767 (3) | 0.5378 (6) | 0.4617 (4) | 0.0377 (12) |
| H2 | 0.699 (4) | 0.569 (9) | 0.516 (4) | 0.03 (2)* |
| O3 | 0.7303 (3) | 0.1975 (5) | 0.3875 (3) | 0.0324 (10) |
| O4 | 0.5788 (4) | 0.1691 (7) | 0.4309 (4) | 0.0385 (12) |
| C1 | 0.5990 (5) | 0.6178 (9) | 0.4009 (6) | 0.0345 (18) |
| C2 | 0.6314 (5) | 0.2287 (7) | 0.3804 (5) | 0.0255 (15) |
| C3 | 0.5581 (5) | 0.5282 (9) | 0.3075 (6) | 0.0307 (17) |
| C4 | 0.5732 (5) | 0.3475 (9) | 0.2962 (5) | 0.0297 (17) |
| C5 | 0.5343 (5) | 0.2691 (11) | 0.2082 (5) | 0.044 (2) |
| H5 | 0.5446 | 0.1504 | 0.2013 | 0.053* |
| C6 | 0.4791 (6) | 0.3685 (13) | 0.1293 (6) | 0.056 (3) |
| H6 | 0.4520 | 0.3151 | 0.0704 | 0.067* |
| C7 | 0.4648 (6) | 0.5461 (13) | 0.1385 (7) | 0.056 (2) |
| H7 | 0.4297 | 0.6127 | 0.0859 | 0.067* |
| C8 | 0.5031 (5) | 0.6231 (10) | 0.2269 (6) | 0.043 (2) |
| H8 | 0.4920 | 0.7418 | 0.2329 | 0.052* |
| C9 | 0.3276 (4) | 0.0844 (8) | 0.3171 (4) | 0.0305 (15) |
| C10 | 0.3175 (5) | 0.2651 (8) | 0.3301 (5) | 0.0342 (16) |
| H10 | 0.3433 | 0.3149 | 0.3901 | 0.041* |
| C11 | 0.2688 (4) | 0.3668 (9) | 0.2525 (5) | 0.0403 (17) |
| H11 | 0.2614 | 0.4862 | 0.2598 | 0.048* |
| C12 | 0.2314 (5) | 0.2920 (9) | 0.1649 (5) | 0.0378 (17) |
| C13 | 0.2417 (5) | 0.1129 (9) | 0.1509 (5) | 0.0425 (17) |
| H13 | 0.2166 | 0.0638 | 0.0908 | 0.051* |
| C14 | 0.2908 (4) | 0.0107 (8) | 0.2296 (5) | 0.0356 (16) |
| H14 | 0.2983 | -0.1086 | 0.2223 | 0.043* |

supplementary materials

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|------------|------------|------------|-------------|-------------|------------|
| Br1 | 0.0717 (5) | 0.0667 (6) | 0.0567 (5) | 0.0124 (6) | 0.0056 (3) | 0.0159 (6) |
| N1 | 0.033 (2) | 0.020 (3) | 0.047 (3) | -0.002 (2) | 0.013 (2) | -0.003 (2) |
| O1 | 0.052 (3) | 0.027 (3) | 0.082 (4) | 0.015 (2) | 0.011 (3) | -0.012 (3) |
| O2 | 0.035 (2) | 0.024 (2) | 0.045 (3) | 0.0035 (19) | -0.002 (2) | -0.009 (2) |
| O3 | 0.025 (2) | 0.021 (2) | 0.050 (3) | 0.0016 (17) | 0.0098 (19) | 0.001 (2) |
| O4 | 0.033 (2) | 0.040 (3) | 0.043 (3) | -0.007 (2) | 0.013 (2) | 0.004 (2) |
| C1 | 0.019 (3) | 0.030 (4) | 0.055 (5) | 0.002 (3) | 0.011 (3) | 0.005 (3) |
| C2 | 0.029 (4) | 0.011 (3) | 0.036 (4) | -0.002 (2) | 0.008 (3) | -0.007 (2) |
| C3 | 0.016 (3) | 0.036 (4) | 0.040 (4) | 0.004 (3) | 0.007 (3) | 0.007 (3) |
| C4 | 0.032 (4) | 0.022 (4) | 0.034 (5) | -0.004 (3) | 0.006 (3) | 0.007 (3) |
| C5 | 0.043 (4) | 0.043 (5) | 0.044 (5) | -0.007 (3) | 0.009 (4) | -0.004 (4) |
| C6 | 0.043 (4) | 0.074 (7) | 0.044 (5) | -0.013 (4) | 0.001 (4) | -0.002 (4) |
| C7 | 0.039 (4) | 0.066 (7) | 0.054 (6) | -0.008 (4) | -0.001 (4) | 0.017 (5) |
| C8 | 0.033 (4) | 0.027 (4) | 0.063 (6) | 0.003 (3) | 0.003 (4) | 0.014 (4) |
| C9 | 0.021 (3) | 0.035 (4) | 0.037 (4) | -0.003 (3) | 0.010 (3) | 0.008 (3) |
| C10 | 0.032 (3) | 0.030 (4) | 0.038 (4) | -0.002 (3) | 0.005 (3) | -0.004 (3) |
| C11 | 0.036 (3) | 0.034 (4) | 0.050 (5) | 0.005 (3) | 0.012 (3) | 0.005 (3) |
| C12 | 0.033 (3) | 0.041 (5) | 0.038 (4) | 0.003 (3) | 0.007 (3) | 0.008 (3) |
| C13 | 0.036 (4) | 0.052 (5) | 0.038 (4) | -0.004 (3) | 0.008 (3) | -0.007 (3) |
| C14 | 0.037 (3) | 0.024 (4) | 0.045 (4) | 0.000 (3) | 0.012 (3) | -0.006 (3) |

Geometric parameters (\AA , $^\circ$)

| | | | |
|------------|------------|----------|------------|
| Br1—C12 | 1.927 (6) | C5—H5 | 0.9300 |
| N1—C9 | 1.468 (8) | C6—C7 | 1.386 (12) |
| N1—H1A | 0.8900 | C6—H6 | 0.9300 |
| N1—H1B | 0.8900 | C7—C8 | 1.382 (11) |
| N1—H1C | 0.8900 | C7—H7 | 0.9300 |
| O1—C1 | 1.238 (8) | C8—H8 | 0.9300 |
| O2—C1 | 1.299 (8) | C9—C14 | 1.359 (8) |
| O2—H2 | 0.80 (6) | C9—C10 | 1.410 (9) |
| O3—C2 | 1.292 (7) | C10—C11 | 1.377 (9) |
| O4—C2 | 1.236 (8) | C10—H10 | 0.9300 |
| C1—C3 | 1.490 (11) | C11—C12 | 1.365 (9) |
| C2—C4 | 1.548 (9) | C11—H11 | 0.9300 |
| C3—C8 | 1.400 (10) | C12—C13 | 1.400 (10) |
| C3—C4 | 1.415 (8) | C13—C14 | 1.392 (9) |
| C4—C5 | 1.385 (11) | C13—H13 | 0.9300 |
| C5—C6 | 1.402 (12) | C14—H14 | 0.9300 |
| C9—N1—H1A | 109.5 | C8—C7—C6 | 119.2 (9) |
| C9—N1—H1B | 109.5 | C8—C7—H7 | 120.4 |
| H1A—N1—H1B | 109.5 | C6—C7—H7 | 120.4 |
| C9—N1—H1C | 109.5 | C7—C8—C3 | 122.2 (8) |
| H1A—N1—H1C | 109.5 | C7—C8—H8 | 118.9 |

| | | | |
|-------------|------------|-----------------|------------|
| H1B—N1—H1C | 109.5 | C3—C8—H8 | 118.9 |
| C1—O2—H2 | 122 (5) | C14—C9—C10 | 121.0 (6) |
| O1—C1—O2 | 123.2 (7) | C14—C9—N1 | 120.1 (6) |
| O1—C1—C3 | 121.9 (7) | C10—C9—N1 | 118.9 (6) |
| O2—C1—C3 | 114.8 (6) | C11—C10—C9 | 118.9 (6) |
| O4—C2—O3 | 127.0 (6) | C11—C10—H10 | 120.5 |
| O4—C2—C4 | 117.8 (6) | C9—C10—H10 | 120.5 |
| O3—C2—C4 | 115.2 (5) | C12—C11—C10 | 119.9 (6) |
| C8—C3—C4 | 117.7 (8) | C12—C11—H11 | 120.1 |
| C8—C3—C1 | 120.1 (7) | C10—C11—H11 | 120.1 |
| C4—C3—C1 | 122.2 (7) | C11—C12—C13 | 121.8 (6) |
| C5—C4—C3 | 120.5 (8) | C11—C12—Br1 | 119.8 (5) |
| C5—C4—C2 | 117.1 (6) | C13—C12—Br1 | 118.4 (5) |
| C3—C4—C2 | 122.4 (7) | C14—C13—C12 | 118.1 (6) |
| C4—C5—C6 | 120.0 (8) | C14—C13—H13 | 121.0 |
| C4—C5—H5 | 120.0 | C12—C13—H13 | 121.0 |
| C6—C5—H5 | 120.0 | C9—C14—C13 | 120.4 (6) |
| C7—C6—C5 | 120.3 (9) | C9—C14—H14 | 119.8 |
| C7—C6—H6 | 119.8 | C13—C14—H14 | 119.8 |
| C5—C6—H6 | 119.8 | | |
| O1—C1—C3—C8 | 18.0 (10) | C5—C6—C7—C8 | -1.6 (13) |
| O2—C1—C3—C8 | -157.9 (6) | C6—C7—C8—C3 | 1.3 (12) |
| O1—C1—C3—C4 | -162.5 (7) | C4—C3—C8—C7 | -0.3 (10) |
| O2—C1—C3—C4 | 21.7 (9) | C1—C3—C8—C7 | 179.3 (7) |
| C8—C3—C4—C5 | -0.2 (10) | C14—C9—C10—C11 | 0.4 (9) |
| C1—C3—C4—C5 | -179.8 (6) | N1—C9—C10—C11 | -177.8 (5) |
| C8—C3—C4—C2 | -179.1 (5) | C9—C10—C11—C12 | 0.0 (9) |
| C1—C3—C4—C2 | 1.3 (10) | C10—C11—C12—C13 | -0.5 (10) |
| O4—C2—C4—C5 | -95.0 (7) | C10—C11—C12—Br1 | 179.2 (4) |
| O3—C2—C4—C5 | 82.4 (7) | C11—C12—C13—C14 | 0.7 (9) |
| O4—C2—C4—C3 | 83.9 (8) | Br1—C12—C13—C14 | -179.0 (4) |
| O3—C2—C4—C3 | -98.7 (7) | C10—C9—C14—C13 | -0.2 (8) |
| C3—C4—C5—C6 | -0.1 (11) | N1—C9—C14—C13 | 178.0 (5) |
| C2—C4—C5—C6 | 178.9 (6) | C12—C13—C14—C9 | -0.3 (9) |
| C4—C5—C6—C7 | 1.0 (12) | | |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|----------------------------|-------------|---------------|-----------------------|-------------------------|
| O2—H2...O3 ⁱ | 0.80 (6) | 1.76 (6) | 2.518 (6) | 158 (7) |
| N1—H1C...O4 | 0.89 | 2.37 | 2.962 (7) | 125 |
| N1—H1C...O1 ⁱⁱ | 0.89 | 2.13 | 2.916 (7) | 147 |
| N1—H1B...O4 ⁱⁱⁱ | 0.89 | 1.96 | 2.804 (7) | 159 |
| N1—H1A...O3 ^{iv} | 0.89 | 1.96 | 2.828 (6) | 164 |

Symmetry codes: (i) $-x+3/2, y+1/2, -z+1$; (ii) $x, y-1, z$; (iii) $-x+1, y, -z+1$; (iv) $x-1/2, y-1/2, z$.

Fig. 1

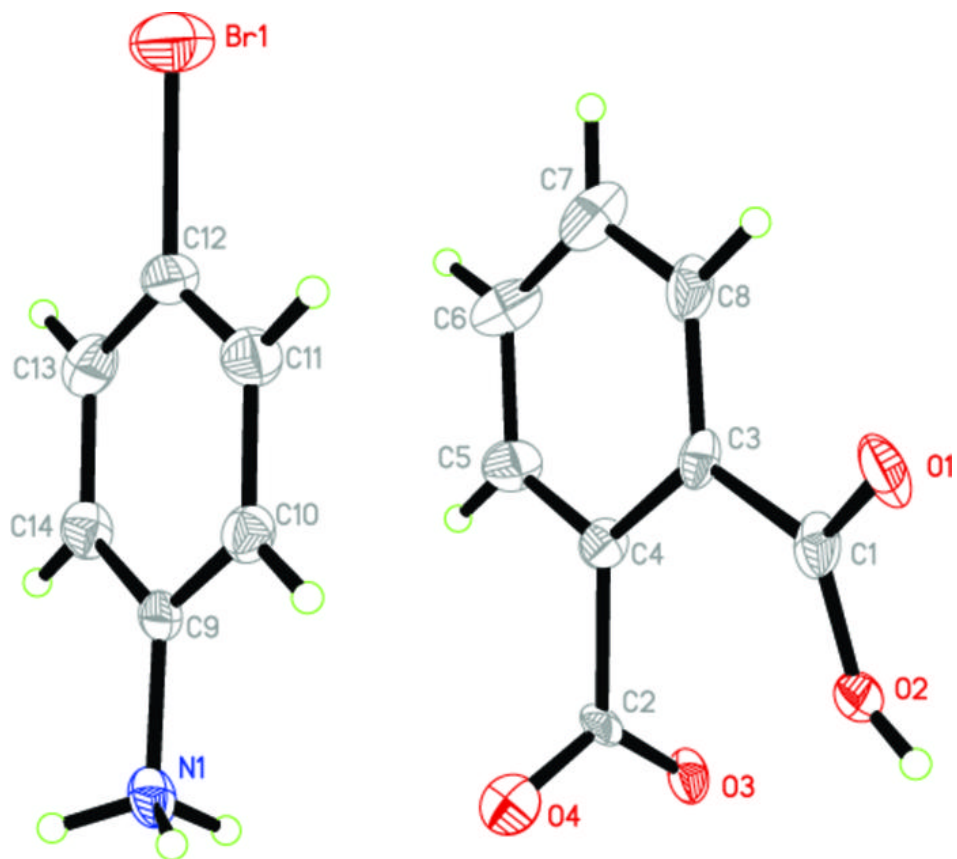


Fig. 2

