2′-Amino-5′-bromoacetophenone
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The synthesis and structure of a brominated derivative of 2'-aminoacetophenone, C₈H₈BrNO, is described. The conformation observed in the solid state was found to be the same as that previously determined by NMR studies.

Comment

As part of a project to prepare novel analogues of the cytotoxic marine alkaloid ascididemin (Lindsay et al., 2000), we required derivatives of 2'-aminoacetophenone. Mild bromination of 2'-aminoacetophenone with pyridinium tribromide (Fieser & Fieser, 1967) afforded the desired product, 2'-amino-5'-bromoacetophenone (I). The conformation of the molecule (Fig. 1) was shown to have the carbonyl group directed towards the amino group so as to maximize H-bonding, and the acetyl methyl group directed towards H-6. A similar solution conformation for this compound has been previously deduced by NMR (Batts et al., 1977).

There is an intramolecular hydrogen bond (Table 1) between an amine proton and the carbonyl O atom, N⋯O 2.679 (3) Å. There is an additional weak interaction between the other amine proton and the ketone oxygen of an adjacent molecule, N⋯O 3.177 (3) Å.

Experimental

Reaction of 2'-aminoacetophenone with pyridinium tribromide (Fieser & Fieser, 1967) in CH₂Cl₂ yielded 2'-amino-5'-bromoacetophenone (80%) with only trace amounts of the dibrominated product 2'-amino-3',5'-dibromoacetophenone being present (Baker et al., 2001). Chromatography on silica gel (CH₂Cl₂–hexane) afforded pure title compound that was recrystallized from EtOH as pale yellow tablets. M.p. 355–356 K [literature (Simpson et al., 1945) 357–358 K, (Gibson & Levin, 1931) and 359–361 K]. ¹H NMR (CDCl₃, 200 MHz) δ 7.77 (1H, d, J = 2.2 Hz, H-6), 7.29 (1H, dd, J = 8.8, 2.2 Hz, H-4), 6.53 (1H, d, J = 8.8 Hz, H-3), 6.16 (2H, bs, NH₂), 2.53 (3H, s, Ac). ¹³C NMR (CDCl₃, 50 MHz) δ 199.4 (C-7), 148.9 (C-2), 136.7 (C-4), 133.8 (C-6), 119.0 (C-1), 118.7 (C-3), 106.2 (C-5), 27.5 (C-8). EIMS 215 / 213 (100%), 200 / 198, 172 / 170. HREIMS m/z 214.9773 (calculated for C₈H₈BrNO, 214.9769), 212.9794 (calculated for C₈H₇BrNO, 212.9789). Analysis calculated for C₈H₇BrNO: C, 44.89; H, 3.77; N, 4.28. 

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6.54; found C, 44.82; H, 3.51; N, 6.61%.

Crystal data

\[ \text{C}_8\text{H}_8\text{BrNO} \]

\[ \text{Mr} = 214.06 \]

Orthorhombic, \( Pnna \)

\[ a = 21.9206 (6) \text{ Å} \]

\[ b = 7.3583 (2) \text{ Å} \]

\[ c = 5.0596 (2) \text{ Å} \]

\[ V = 816.11 (4) \text{ Å}^3 \]

\[ Z = 4 \]

\[ D_\text{x} = 1.742 \text{ Mg m}^{-3} \]

Data collection

Siemens SMART diffractometer

Area detector \( o \)-scans

Absorption correction: multi-scan

\( T_{\text{min}} = 0.229, \ T_{\text{max}} = 0.468 \)

4318 measured reflections

1347 independent reflections

Mo \( K\alpha \) radiation

Cell parameters from 3623 reflections

\[ \theta = 2-25^\circ \]

\[ \mu = 4.97 \text{ mm}^{-1} \]

\[ T = 291 (2) \text{ K} \]

Prism, yellow

0.42 \times 0.22 \times 0.18 \text{ mm}

Refinement

Refinement on \( F^2 \)

\[ R(F^2) = 0.024 \]

\[ wR(F^2) = 0.061 \]

\[ S = 1.08 \]

1347 reflections

124 parameters

H atoms treated by a mixture of constrained and independent refinement

\[ w = \frac{1}{[\sigma^2(F^2) + (0.0374P)^2 + 0.0296P]} \]

where \( P = (F^2 + 2F_c^2)/3 \)

\[ (\Delta / \sigma)_{\text{max}} = 0.007 \]

\[ \Delta \rho_{\text{max}} = 0.18 \text{ e Å}^{-3} \]

\[ \Delta \rho_{\text{min}} = -0.41 \text{ e Å}^{-3} \]

Absolute structure: Flack (1983)

Flack parameter = 0.059 (13)

Table 1

Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H—A</th>
<th>D—H</th>
<th>H—A</th>
<th>D···A</th>
<th>D—H···A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N—H Bonds</td>
<td>0.86</td>
<td>2.05</td>
<td>2.676 (3)</td>
<td>129</td>
</tr>
<tr>
<td>N—H Bond</td>
<td>0.86</td>
<td>2.50</td>
<td>3.177 (3)</td>
<td>137</td>
</tr>
</tbody>
</table>

Symmetry code: (i) \( 1-x, -y, z-\frac{1}{2} \)

H atoms were placed geometrically and coordinates, apart from those of the methyl group, allowed to refine with isotropic displacement parameter riding on \( U_{eq} \) of the carrier atom. The methyl group was refined using a riding model.

Data collection: \( SMART \) (Siemens, 1995); cell refinement: \( SMART \); data reduction: \( SAINT \) (Siemens, 1995); program(s) used to solve structure: \( SHELXS \) (Sheldrick, 1990); program(s) used to refine structure: \( SHELXL \) (Sheldrick, 1997); molecular graphics: \( SHELXTL \) (Siemens, 1994); software used to prepare material for publication: \( SHELXL \) 97.

References


