Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2′-Amino-5′-bromoacetophenone

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Received 3 May 2001
Accepted 18 May 2001
Online 22 May 2001

Key indicators

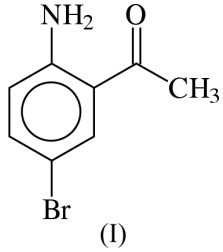
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.003 Å
R factor = 0.024
wR factor = 0.061
Data-to-parameter ratio = 10.9

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

The synthesis and structure of a brominated derivative of 2′-aminoacetophenone, C_8H_8BrNO, 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).



(I)

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 CH_2Cl_2 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 (CH_2Cl_2–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]. ^{1}H NMR ($CDCl_3$, 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*, NH_2), 2.53 (3H, *s*, Ac). ^{13}C NMR ($CDCl_3$, 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 $C_8H_8{}^{81}BrNO$, 214.9769), 212.9794 (calculated for $C_8H_8{}^{79}BrNO$, 212.9789). Analysis calculated for C_8H_8BrNO: C, 44.89; H, 3.77; N,

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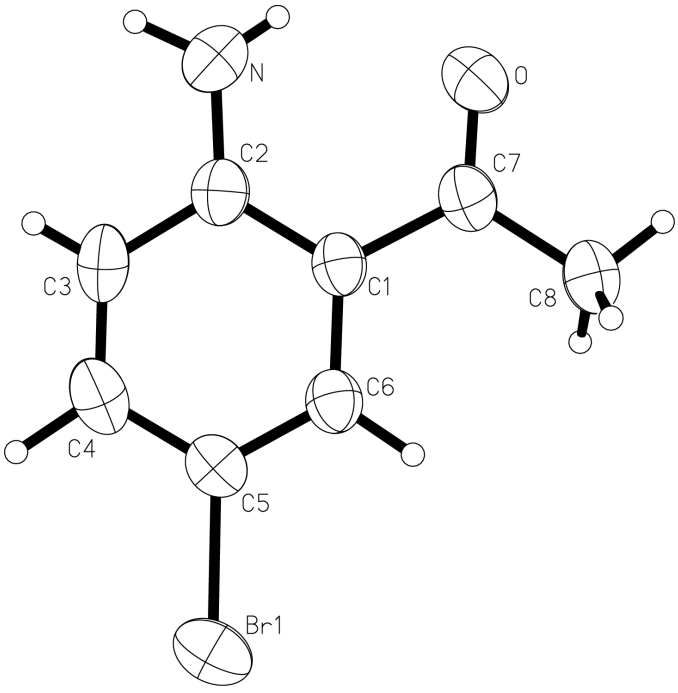

Figure 1
Structure of (I) showing 50% probability displacement ellipsoids and H atoms as arbitary spheres (Siemens, 1994).

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

Crystal data

C_8H_8BrNO
M_r = 214.06
Orthorhombic, $Pna2_1$
a = 21.9206 (6) Å
b = 7.3583 (2) Å
c = 5.0596 (2) Å
V = 816.11 (4) Å^3
Z = 4
D_x = 1.742 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3623 reflections
θ = 2–25°
μ = 4.97 mm^{-1}
T = 291 (2) K
Prism, yellow
0.42 × 0.22 × 0.18 mm

Data collection

Siemens SMART diffractometer
Area detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.229, T_{max} = 0.468
4318 measured reflections
1347 independent reflections
1278 reflections with $I > 2\sigma(I)$
R_{int} = 0.022
θ_{max} = 25.6°
$h = -26 \rightarrow 23$
$k = -8 \rightarrow 8$
$l = -6 \rightarrow 4$
Intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 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
$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.0296P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.007
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}
Absolute structure: Flack (1983)
Flack parameter = 0.059 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H0b···O	0.86	2.05	2.676 (3)	129
N—H0b···O^{i}	0.86	2.50	3.177 (3)	137

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 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*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

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