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2′-Amino-3′,5′-dibromoacetophenone

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Key indicators

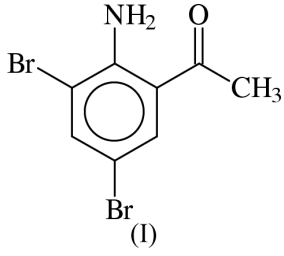
Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.004 Å
R factor = 0.023
wR factor = 0.061
Data-to-parameter ratio = 14.2

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 di-brominated derivative of 2′-aminoacetophenone, $C_8H_7Br_2NO$, is described. The conformation observed in the solid state was found to be the same as that previously proposed for solution conformations of related compounds.

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. Bromination of 2′-aminoacetophenone with excess bromine in acetic acid afforded the desired product, 2′-amino-3′,5′-dibromoacetophenone, (I). As with the related monobromo-derivative 2′-amino-5′-bromoacetophenone (Baker *et al.*, 2001), the conformation of the molecule was shown to have the carbonyl group directed towards the amino group so as to maximize hydrogen bonding, and the acetyl methyl group directed towards H6. Similar solution conformations have been reported for related disubstituted acetophenones (Batts *et al.*, 1977).



The amine protons form strong intramolecular hydrogen bonds (Table 1) to the ketone O and Br atoms, N···O 2.661 (4) and N···Br 3.095 (3) Å. There is an additional weak N···O interaction of 3.110 (3) Å to an adjacent molecule.

Experimental

Reaction of 2′-aminoacetophenone with excess bromine in acetic acid yielded the title compound 2′-amino-3′,5′-dibromoacetophenone. Chromatography on silica gel (CH_2Cl_2–hexane) afforded a pure sample that was recrystallized from EtOH as pale yellow tablets. M.p. 397–399 K [literature (Leonard & Boyd, 1946) 396–397 K and (Fuchs, 1915) 403 K]. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.76 (1H, *d*, J = 2.2 Hz, H-6), 7.64 (1H, *d*, J = 2.2 Hz, H-4), 6.88 (2H, *bs*, NH_2), 2.55 (3H, *s*, Ac). ^{13}C NMR ($CDCl_3$, 50 MHz) δ 198.9 (C-7), 146.2 (C-2), 139.1 (C-4), 133.6 (C-6), 119.6 (C-1), 111.7 (C-5), 105.7 (C-3), 27.9 (C-8). EIMS 295 / 293 / 291 (100%), 280 / 278 / 276, 171 / 169, 170 / 168. HREIMS m/z 294.8853 (calculated for $C_8H_7{}^{81}Br_2NO$, 294.8853), 292.8874 (calculated for $C_8H_7{}^{79}Br^{81}BrNO$, 292.8874), 290.8899 (calculated for $C_8H_7{}^{79}Br_2NO$, 290.8894).

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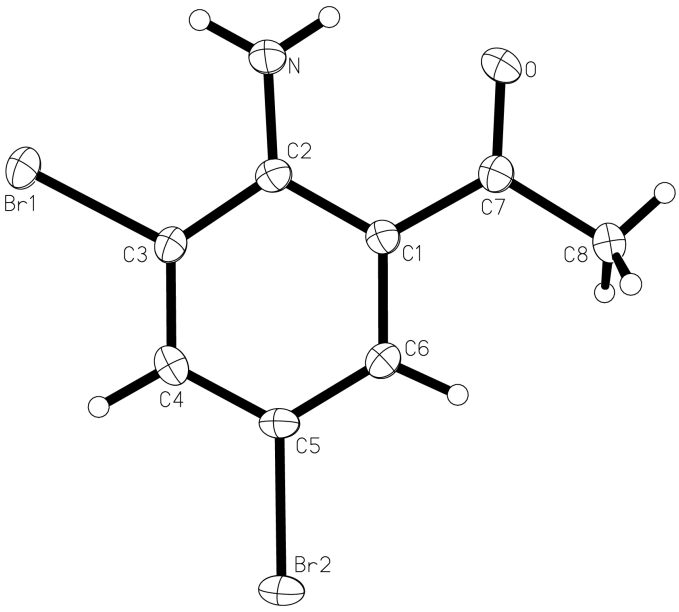

Figure 1
Structure of (I) showing 50% probability displacement ellipsoids for non-H atoms and hydrogen atoms as arbitary spheres (Siemens, 1994).

Crystal data

$C_8H_7Br_2NO$
M_r = 292.97
Monoclinic, $P2_1/c$
a = 9.147 (6) Å
b = 10.138 (7) Å
c = 9.699 (8) Å
β = 92.02 (4)°
V = 898.9 (11) Å^3
Z = 4
D_x = 2.165 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4466 reflections
θ = 2–25°
μ = 8.97 mm^{-1}
T = 203 (2) K
Tablet, yellow
0.35 × 0.25 × 0.25 mm

Data collection

Siemens SMART diffractometer
Area-detector ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.145, T_{max} = 0.213
5582 measured reflections
1582 independent reflections
1444 reflections with $I > 2\sigma(I)$
R_{int} = 0.023
θ_{max} = 25°
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 12$
Intensity decay: < 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.023
$wR(F^2)$ = 0.061
S = 1.06
1841 reflections
130 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0424P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.94 e Å^{-3}
$\Delta\rho_{min}$ = −0.41 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N—H0b···O	0.87	2.01	2.660 (4)	131
N—H0a···O^{i}	0.87	2.30	3.110 (3)	155
N—H0a···Br1	0.87	2.61	3.059 (3)	114

Symmetry code: (i) $1 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

H atoms were placed geometrically and allowed to ride on the carrier atom with isotropic displacement parameter 20% greater than U_{eq} for the the carrier atom (50% for the methyl group).

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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