3-(4-Bromophenyl)-N,N-dimethyl-3-oxopropan-1-aminium chloride

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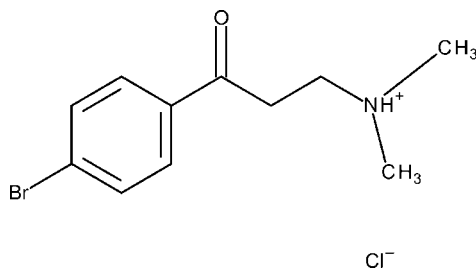Correspondence e-mail: rodrigo.abonia@correounivalle.edu.co

The title compound, $C_{11}H_{15}BrNO^+ \cdot Cl^-$, was obtained as a precursor within our current program for the synthesis of new β-aminoalcohols *via* a Mannich-type reaction. The protonated amino N atom is hydrogen bonded to the chloride anion. With exception of one methyl group, the cation is approximately planar (r.m.s. deviation for all non H-atoms = 0.069 Å).

Related literature

For (*N,N*-dialkylamino)propiophenones, see: Alper *et al.* (2002); Pupo *et al.* (2003); Abonia *et al.* (2004). For details of the synthesis, see: Brandes & Roth (1967); Vogel *et al.* (1978).

Experimental

Crystal data

$C_{11}H_{15}BrNO^+ \cdot Cl^-$	b = 12.5694 (5) Å
M_r = 292.60	c = 10.6483 (5) Å
Monoclinic, $P2_1/c$	β = 115.594 (2)°
a = 10.5050 (8) Å	V = 1268.06 (12) Å^3
Z = 4	T = 295 K
Cu $K\alpha$ radiation	0.44 × 0.26 × 0.26 mm
μ = 6.16 mm^{-1}	

Data collection

Enraf–Nonius CAD-4 diffractometer	2564 measured reflections
Absorption correction: ψ scan (*CORINC*; Dräger & Gattow, 1971)	2564 independent reflections
	2258 reflections with $I > 2\sigma(I)$
T_{min} = 0.61, T_{max} = 1.00	3 standard reflections every 60 min intensity decay: 5%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045	Only H-atom displacement parameters refined
$wR(F^2)$ = 0.123	$\Delta\rho_{max}$ = 0.72 e Å^{-3}
S = 1.12	$\Delta\rho_{min}$ = −0.65 e Å^{-3}
2564 reflections	
146 parameters	

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N10—H10$\cdots$Cl1	1.00	1.99	2.983 (2)	171

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *PLATON*.

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supporting information

3-(4-Bromophenyl)-*N*,*N*-dimethyl-3-oxopropan-1-aminium chloride

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S1. Comment

The classical method for the synthesis of 3-(*N*,*N*-dialkylamino)propiophenone salts is the well known Mannich reaction between an alkyl aryl ketone, dialkylamine hydrochloride and polyformaldehyde in refluxing ethanol (Vogel *et al.*, 1978). In this approach, the *N*,*N*-dialkylmethyleneammonium chloride ($H_2C=NR_2Cl$) is formed *in situ*, which suffers a Michael type addition from the methylene active ketone to render the expected Mannich adduct (Brandes *et al.*, 1967).

The 3-(*N*,*N*-dialkylamino)propiophenone salts are visualized as synthetic equivalents of the less stable and more reactive *α*,*β*-unsaturated aryl vinyl ketones. For instance, they can react with nucleophiles like amines through a Michael type addition which could lead to the formation of *β*-aminoalcohols as is our purpose with compound (I).

In the crystal the title compound adopts an essentially planar structure with a dihedral angle of 5.0 (2)° between the almost planar aminopropane-1-one group (maximal deviation from least square plane 0.038Å at C9) and the phenyl ring. The protonated N10 atom forms a hydrogen bond to Cl1 (N10—H10···Cl1 1.99 Å).

S2. Experimental

A mixture of dimethylamine hydrochloride (2.0 g, 25 mmol), polyformaldehyde (0.754 g, 25 mmol), *p*-bromoaceto-phenone (3.66 g, 9.2 mmol), 95% ethanol (4 mL) and conc HCl (0.02 mL) was heated at reflux in an oil bath during 3 h (Vogel *et al.* (1978)). After complete disappearance of the starting acetophenone, as monitored by thin-layer chromatography, the hot mixture was filtered; acetone (15 mL) was added to the filtrate and cooled into the freezer overnight. The resulting solid was filtered, washed with acetone (2 *x* 5 mL) and dried at ambient temperature affording the title compound (I), as white solid [yield 94%, m.p. 495 K].

Crystals of (I) suitable for single-crystal X-ray diffraction were grown by slow evaporation at ambient temperature and in air, from a 1:1 ethanol:acetone solution.

S3. Refinement

Hydrogen atoms attached to carbons were placed at calculated positions with C—H = 0.95 Å (aromatic) or 0.98–0.99 Å (*sp*³ C-atom). All H atoms were refined in the riding-model approximation with isotropic displacement parameters.
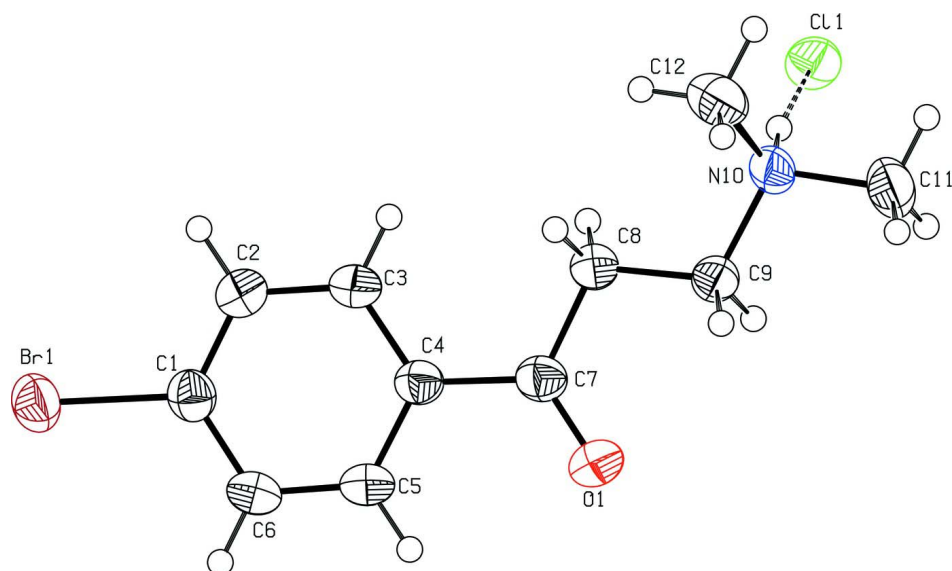
Figure 1

View of compound **I**. Displacement ellipsoids are drawn at the 50% probability level.

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Crystal data

$C_{11}H_{15}BrNO^+ \cdot Cl^-$	$F(000) = 592$
$M_r = 292.60$	$D_x = 1.533$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 495 K
Hall symbol: -P 2ybc	Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å
$a = 10.5050$ (8) Å	Cell parameters from 25 reflections
$b = 12.5694$ (5) Å	$\theta = 64$–74°
$c = 10.6483$ (5) Å	$\mu = 6.16$ mm^{-1}
$\beta = 115.594$ (2)°	$T = 295$ K
$V = 1268.06$ (12) Å^3	Block, brown
$Z = 4$	0.44 × 0.26 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	2564 independent reflections
Radiation source: rotating anode	2258 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.000$
$\theta/2\omega$ scans	$\theta_{max} = 73.8°$, $\theta_{min} = 4.7°$
Absorption correction: ψ scan	$h = -11 \rightarrow 13$
(CORINC; Dräger & Gattow, 1971)	$k = -15 \rightarrow 0$
$T_{min} = 0.61$, $T_{max} = 1.00$	$l = -13 \rightarrow 0$
2564 measured reflections	3 standard reflections every 60 min
	intensity decay: 5%

Refinement

Refinement on F^2	146 parameters
Least-squares matrix: full	0 restraints
$R[F^2 > 2\sigma(F^2)] = 0.045$	Primary atom site location: structure-invariant direct methods
$wR(F^2) = 0.123$	
$S = 1.12$	Secondary atom site location: structure-invariant direct methods
2564 reflections	

Hydrogen site location: difference Fourier map
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0762P)^2 + 0.3958P]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.72$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Extinction coefficient: 0.0047 (5)

Special details

Experimental. IR (KBr disk): 3080, 3024, 2954, 2912, 2628, 2543 (br), 2503, 2440 (br), 1684 (C=O), 1580, 1473, 1391, 1329, 1216, 1065, 1002, 963, 787 cm$^{-1.}$ ^{1}H-NMR (DMSO-d6): 2.79 (s, 6H), 3.39 (t, J = 7.5 Hz, 2H), 3.64 (t, J = 7.2 Hz,2*H*), 7.78 ("d", J =8.4 Hz, 2H), 7.95 ("d", J = 8.4 Hz, 2H), 10.93 (bs, 1H, NH) p.p.m.; ^{13}C-NMR (DMSO-d6): 33.2, 42.1, 51.5, 127.8, 130.0, 131.9, 134.9, 196.0 (C=O) p.p.m..

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.31084 (4)	0.13998 (3)	0.50877 (3)	0.04655 (18)
Cl1	0.89690 (9)	−0.34411 (6)	1.32816 (9)	0.0430 (2)
O1	0.7418 (3)	0.0972 (2)	1.2059 (2)	0.0539 (6)
C1	0.4405 (3)	0.1090 (2)	0.6944 (3)	0.0374 (6)
C2	0.5264 (3)	0.0213 (3)	0.7200 (3)	0.0436 (7)
H2	0.5200	−0.0221	0.6467	0.058 (11)*
C3	0.6223 (3)	−0.0025 (3)	0.8549 (3)	0.0411 (7)
H3	0.6794	−0.0623	0.8722	0.040 (9)*
C4	0.6335 (3)	0.0629 (2)	0.9646 (3)	0.0335 (6)
C5	0.5434 (4)	0.1497 (2)	0.9364 (4)	0.0419 (7)
H5	0.5478	0.1922	1.0097	0.060 (11)*
C6	0.4478 (4)	0.1745 (3)	0.8029 (3)	0.0430 (7)
H6	0.3893	0.2336	0.7854	0.054 (11)*
C7	0.7377 (3)	0.0416 (2)	1.1111 (3)	0.0362 (6)
C8	0.8395 (3)	−0.0495 (2)	1.1373 (3)	0.0369 (6)
H8A	0.7874	−0.1160	1.1125	0.058 (8)*
H8B	0.8885	−0.0414	1.0788	0.058 (8)*
C9	0.9456 (3)	−0.0535 (2)	1.2878 (3)	0.0360 (6)
H9A	0.9986	0.0126	1.3113	0.046 (7)*
H9B	0.8957	−0.0590	1.3459	0.046 (7)*
N10	1.0466 (3)	−0.14452 (17)	1.3199 (3)	0.0358 (6)
H10	0.9959	−0.2136	1.3123	0.053 (11)*
C11	1.1447 (5)	−0.1452 (3)	1.4695 (4)	0.0578 (11)
H11A	1.2084	−0.2042	1.4889	0.082 (10)*
H11B	1.0919	−0.1518	1.5236	0.082 (10)*
H11C	1.1974	−0.0800	1.4932	0.082 (10)*
C12	1.1245 (4)	−0.1462 (3)	1.2322 (4)	0.0526 (9)

H12A	1.0585	−0.1462	1.1357	0.101 (11)*
H12B	1.1817	−0.2092	1.2524	0.101 (11)*
H12C	1.1838	−0.0845	1.2518	0.101 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0519 (3)	0.0423 (2)	0.0400 (2)	0.00146 (13)	0.01472 (18)	0.00820 (13)
Cl1	0.0541 (5)	0.0294 (4)	0.0461 (4)	−0.0091 (3)	0.0223 (4)	−0.0025 (3)
O1	0.0644 (15)	0.0500 (14)	0.0408 (12)	0.0130 (12)	0.0166 (12)	−0.0113 (11)
C1	0.0398 (15)	0.0351 (15)	0.0376 (15)	−0.0020 (12)	0.0170 (13)	0.0041 (12)
C2	0.0492 (18)	0.0441 (18)	0.0381 (15)	0.0058 (14)	0.0193 (14)	−0.0037 (13)
C3	0.0436 (16)	0.0380 (16)	0.0418 (16)	0.0102 (13)	0.0187 (14)	−0.0025 (13)
C4	0.0364 (14)	0.0294 (14)	0.0363 (14)	0.0003 (11)	0.0170 (12)	−0.0011 (11)
C5	0.0505 (18)	0.0309 (16)	0.0444 (18)	0.0058 (12)	0.0206 (15)	−0.0055 (12)
C6	0.0519 (19)	0.0291 (15)	0.0471 (18)	0.0082 (13)	0.0206 (15)	−0.0004 (13)
C7	0.0401 (15)	0.0284 (13)	0.0406 (15)	−0.0010 (11)	0.0181 (13)	−0.0009 (12)
C8	0.0418 (15)	0.0318 (15)	0.0347 (14)	0.0019 (12)	0.0142 (12)	−0.0018 (11)
C9	0.0467 (16)	0.0270 (14)	0.0339 (14)	−0.0007 (12)	0.0170 (13)	0.0003 (11)
N10	0.0458 (14)	0.0228 (11)	0.0342 (13)	−0.0019 (9)	0.0130 (11)	0.0029 (9)
C11	0.070 (2)	0.0371 (19)	0.0411 (19)	0.0028 (16)	0.0002 (18)	0.0031 (14)
C12	0.057 (2)	0.044 (2)	0.063 (2)	0.0121 (15)	0.0319 (19)	0.0101 (16)

Geometric parameters (Å, °)

Br1—C1	1.894 (3)	C2—H2	0.9300
O1—C7	1.213 (4)	C3—H3	0.9300
C1—C2	1.375 (4)	C5—H5	0.9300
C1—C6	1.394 (4)	C6—H6	0.9300
C2—C3	1.385 (4)	C8—H8A	0.9700
C3—C4	1.391 (4)	C8—H8B	0.9700
C4—C5	1.390 (4)	C9—H9A	0.9700
C4—C7	1.493 (4)	C9—H9B	0.9700
C5—C6	1.376 (5)	C11—H11A	0.9600
C7—C8	1.509 (4)	C11—H11B	0.9600
C8—C9	1.507 (4)	C11—H11C	0.9600
C9—N10	1.496 (4)	C12—H12A	0.9600
N10—C11	1.477 (4)	C12—H12B	0.9600
N10—C12	1.484 (5)	C12—H12C	0.9600
N10—H10	1.0000		
C2—C1—C6	120.9 (3)	C1—C6—H6	121.00
C2—C1—Br1	119.1 (2)	C5—C6—H6	121.00
C6—C1—Br1	120.0 (2)	C7—C8—H8A	109.00
C1—C2—C3	120.0 (3)	C7—C8—H8B	109.00
C2—C3—C4	120.2 (3)	C9—C8—H8A	109.00
C5—C4—C3	118.7 (3)	C9—C8—H8B	109.00
C5—C4—C7	119.3 (3)	H8A—C8—H8B	108.00

C3—C4—C7	122.0 (3)	N10—C9—H9A	109.00
C6—C5—C4	121.7 (3)	N10—C9—H9B	109.00
C5—C6—C1	118.5 (3)	C8—C9—H9A	109.00
O1—C7—C4	120.9 (3)	C8—C9—H9B	109.00
O1—C7—C8	121.1 (3)	H9A—C9—H9B	108.00
C4—C7—C8	118.0 (2)	N10—C11—H11A	109.00
C9—C8—C7	111.2 (2)	N10—C11—H11B	109.00
N10—C9—C8	113.2 (2)	N10—C11—H11C	109.00
C11—N10—C12	111.2 (3)	H11A—C11—H11B	109.00
C11—N10—C9	110.2 (2)	H11A—C11—H11C	110.00
C12—N10—C9	113.4 (2)	H11B—C11—H11C	109.00
C1—C2—H2	120.00	N10—C12—H12A	110.00
C3—C2—H2	120.00	N10—C12—H12B	109.00
C2—C3—H3	120.00	N10—C12—H12C	110.00
C4—C3—H3	120.00	H12A—C12—H12B	109.00
C4—C5—H5	119.00	H12A—C12—H12C	109.00
C6—C5—H5	119.00	H12B—C12—H12C	109.00
C6—C1—C2—C3	−0.5 (5)	C5—C4—C7—O1	2.1 (5)
Br1—C1—C2—C3	179.7 (3)	C3—C4—C7—O1	−177.0 (3)
C1—C2—C3—C4	−0.8 (5)	C5—C4—C7—C8	−176.6 (3)
C2—C3—C4—C5	2.3 (5)	C3—C4—C7—C8	4.2 (4)
C2—C3—C4—C7	−178.6 (3)	O1—C7—C8—C9	−4.1 (4)
C3—C4—C5—C6	−2.5 (5)	C4—C7—C8—C9	174.6 (2)
C7—C4—C5—C6	178.4 (3)	C7—C8—C9—N10	178.4 (2)
C4—C5—C6—C1	1.2 (5)	C8—C9—N10—C11	−178.4 (3)
C2—C1—C6—C5	0.3 (5)	C8—C9—N10—C12	56.2 (4)
Br1—C1—C6—C5	−179.9 (2)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10···Cl1	1.00	1.99	2.983 (2)	171