

1-[2-(Biphenyl-4-yl)-2-oxoethyl]-4-(*N,N*-dimethyl-
amino)pyridinium bromide hemihydrateT. V. Sundar,^a V. Parthasarathi,^{a*}
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The title compound, $C_{21}H_{21}N_2O^+ \cdot Br^- \cdot 0.5H_2O$, crystallizes in a monoclinic unit cell with two cations, two anions and one water molecule in the asymmetric unit. The conformations of the two independent cations are different. The crystal packing is stabilized by $O-H \cdots Br$ and $C-H \cdots Br$ interactions and weak intermolecular $C-H \cdots O$ hydrogen bonds.

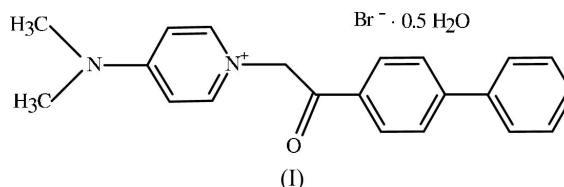
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Comment

4-Dimethylaminopyridine (DMAP) is a well known catalyst for a variety of synthetic transformations under mild conditions (Prabakaran *et al.*, 2001, and references therein; Sundar *et al.*, 2004). In a continuation of the identification of bioactive compounds, the structure determination of the title compound, (I), was undertaken.



Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
 Mean $\sigma(C-C) = 0.006\text{ \AA}$
 R factor = 0.056
 wR factor = 0.140
 Data-to-parameter ratio = 16.9

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

The asymmetric unit of (I) contains two crystallographically independent cations, *A* and *B*, two anions and one water molecule (Fig. 1). The bond lengths and angles in the DMAP moieties of *A* and *B* (Table 1) are comparable with those reported for related structures (Sundar *et al.*, 2004). The angles between the least-squares planes of the dimethylamino moiety and the pyridine ring in cations *A* and *B* are 10.6 (2) and

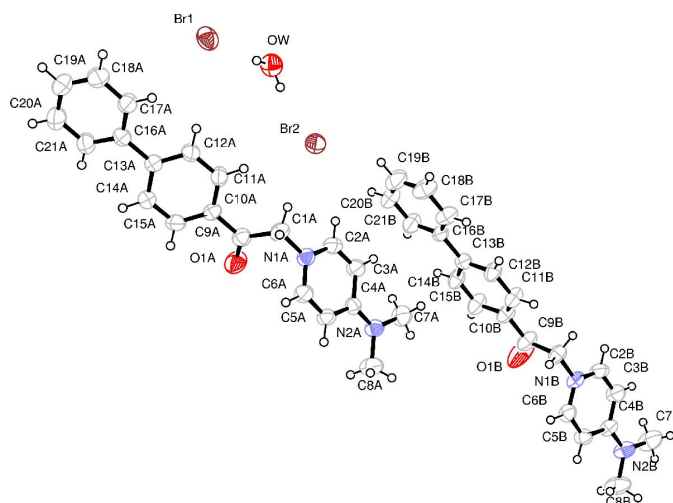


Figure 1

The asymmetric unit of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of arbitrary radii.

13.3 (2)°, respectively. The dihedral angles between the mean planes of the benzene rings in *A* and *B* are 15.7 (2) and 1.5 (2)°, respectively. In cation *A*, the angle between the least-squares planes of the pyridine ring and biphenyl moiety is 50.2 (1)°, whereas in cation *B*, the corresponding angle is 86.34 (12)°, close to the values of 81.01 (11) and 78.64 (13)° observed in related structures (Sundar *et al.*, 2004). Fig. 2 shows a superposition of cations *A* and *B*. The r.m.s. deviations of the superimposed separate DMAP and biphenyl moieties are 0.06 and 0.13 Å, respectively. The overall r.m.s. deviation of cations *A* and *B* is 0.34 Å. The main conformational differences in *A* and *B* are around the biphenyl moieties (Fig. 2), which may be caused by the packing interactions.

The pyridinium systems in cations *A* and *B* have a substantial degree of quinoidal character, since the bond lengths C2–C3 and C5–C6 in both cations (*ca* 1.35 Å; Table 1) are significantly shorter than those observed for C3–C4 and C4–C5 bonds (*ca* 1.41 Å). The C4–N2 bond lengths (Table 1) are intermediate between the typical C–N single- and double-bond distances (Allen *et al.*, 1987), indicating significant conjugation. The sum of the bond angles around atoms N1 and N2 in both cations is close to 360° (Table 1), hence there is no evidence for an *sp*³ lone pair. The crystal packing (Fig. 3) is stabilized by O–H···Br and C–H···Br interactions and weak intermolecular C–H···O hydrogen bonds (Table 2).

Experimental

A solution of 4-phenylphenacyl bromide (1.6 g, 4 mmol) and DMAP (0.5 g, 4 mmol) in dry acetone was refluxed for 30 min. After cooling to room temperature (303 K), the solid that separated was filtered off and washed with dry acetone to give the stable salt (I) (yield 1.87 g, 89%; m.p. 519–521 K), which was recrystallized from ethanol.

Crystal data

C ₂₁ H ₂₁ N ₂ O ⁺ ·Br ⁻ ·0.5H ₂ O	<i>D</i> _x = 1.384 Mg m ⁻³
<i>M</i> _r = 406.32	Mo Kα radiation
Monoclinic, <i>C</i> 2/ <i>c</i>	Cell parameters from 911 reflections
<i>a</i> = 21.077 (6) Å	<i>θ</i> = 2.2–27.8°
<i>b</i> = 9.971 (3) Å	<i>μ</i> = 2.12 mm ⁻¹
<i>c</i> = 37.485 (12) Å	<i>T</i> = 298 (2) K
<i>β</i> = 98.121 (9)°	Block, colourless
<i>V</i> = 7799 (4) Å ³	0.7 × 0.4 × 0.4 mm
<i>Z</i> = 16	

Data collection

Bruker SMART CCD 1K diffractometer	7982 independent reflections
<i>ω</i> scans	4222 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	<i>R</i> _{int} = 0.088
<i>T</i> _{min} = 0.281, <i>T</i> _{max} = 0.428	<i>θ</i> _{max} = 26.4°
31162 measured reflections	<i>h</i> = -26 → 26
	<i>k</i> = 0 → 12
	<i>l</i> = 0 → 46

Refinement

Refinement on <i>F</i> ²	$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 4.0141P]$
$R[F^2 > 2\sigma(F^2)] = 0.056$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.140$	(Δ/σ) _{max} = 0.001
<i>S</i> = 1.01	Δρ _{max} = 0.52 e Å ⁻³
7982 reflections	Δρ _{min} = -0.34 e Å ⁻³
471 parameters	
H atoms treated by a mixture of independent and constrained refinement	

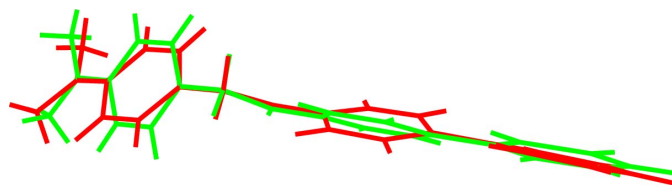


Figure 2
Superimposed fit of cations *A* (red) and *B* (green) of (I).

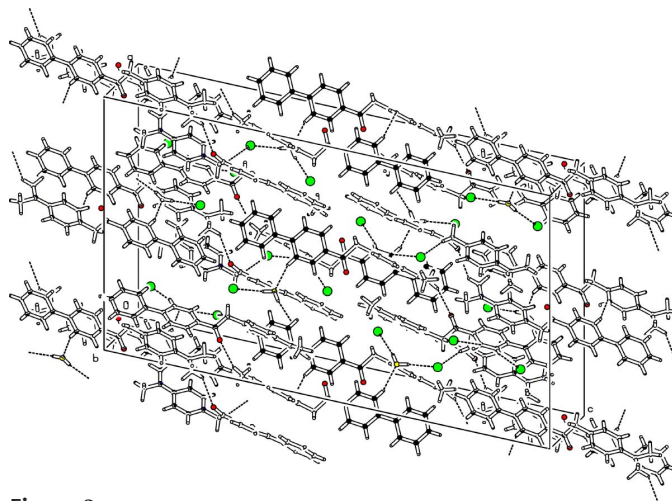


Figure 3
The crystal packing of (I). Intermolecular hydrogen bonds are indicated by dashed lines.

Table 1

Selected geometric parameters (Å, °).

N2A–C4A	1.336 (5)	N2B–C4B	1.327 (5)
C2A–C3A	1.347 (5)	C2B–C3B	1.345 (6)
C3A–C4A	1.428 (6)	C3B–C4B	1.405 (6)
C2A–N1A–C6A	117.7 (4)	C6B–N1B–C2B	118.3 (3)
C2A–N1A–C1A	121.6 (4)	C6B–N1B–C1B	120.6 (4)
C6A–N1A–C1A	120.7 (4)	C2B–N1B–C1B	121.0 (4)
C4A–N2A–C7A	122.4 (4)	C4B–N2B–C7B	122.2 (4)
C4A–N2A–C8A	121.2 (4)	C4B–N2B–C8B	122.0 (4)
C7A–N2A–C8A	116.4 (3)	C7B–N2B–C8B	115.7 (4)

Table 2

Hydrogen-bonding 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>
C1A–H1A···Br2	0.97	2.76	3.713 (5)	170
OW–H22···Br1	0.86	2.47	3.314 (4)	170
OW–H23···Br2	0.87	2.45	3.311 (4)	169
C1A–H1B···Br2 ⁱ	0.97	2.74	3.581 (5)	146
C14A–H14A···OW ⁱⁱ	0.93	2.61	3.530 (6)	173
C21A–H21A···OW ⁱⁱ	0.93	2.62	3.500 (6)	157
C1B–H1D···Br1 ⁱⁱⁱ	0.97	2.92	3.840 (5)	158
C8B–H8D···Br2 ⁱⁱⁱ	0.96	2.80	3.680 (5)	153
C14B–H14B···OW ^{iv}	0.93	2.38	3.270 (6)	160

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

The water H atoms were located in a difference Fourier map and refined with H22–OW and H23–OW distance restraints of 0.86 (1) Å. The remaining H atoms were treated as riding, with C–H = 0.93–0.98 Å and *U*_{iso}(H) = 1.5 or 1.2*U*_{eq}(C).

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINTE* (Bruker, 2000); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PARST* (Nardelli, 1995).

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References

- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
- Bruker (2000). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Prabakaran, P., Thomas Muthaiah, P., Nallu, M., Sathiskumar, V., Bocelli, G. & Rifhi, L. (2001). *J. Chem. Res. (S)*, pp. 248–249.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Sundar, T. V., Parthasarathi, V., Sarkunam, K., Nallu, M., Walfort, B. & Lang, H. (2004). *Acta Cryst.* **C60**, o464–o466.