Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

1-Benzyl-4,5-diphenyl-3-vinylimidazolium bromide

Robert T. Stibrany, Joseph A. Potenza* and Harvey J. Schugar

Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, 610 Taylor Road, Piscataway, New Jersey 08854, USA

Correspondence e-mail:
potenza@rutchem.rutgers.edu

Received 25 June 2002
Accepted 10 July 2002
Online 19 July 2002

Key indicators

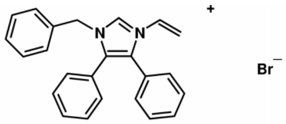
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.009 Å
R factor = 0.043
wR factor = 0.105
Data-to-parameter ratio = 12.4

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

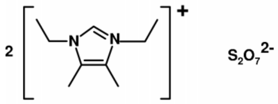
The title compound, $C_{24}H_{21}N_2^+\cdot Br^-$, contains columns of tetrasubstituted imidazolium cations linked to Br^- ions *via* hydrogen bonding. There is little evidence of π-stacking between cations.

Comment

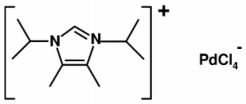
Imidazolium (im) salts, some with melting points well below room temperature, constitute a class of ionic liquids, species that have been used as non-volatile solvents for a number of chemical applications (Welton, 1999). Factors influencing the melting points of these salts include charge delocalization, interionic hydrogen bonding, symmetry, and substituent chain length (Bonhote *et al.*, 1996; Golding *et al.*, 1998). This diversity makes melting points difficult to predict, although charge localization, hydrogen bonding and high symmetry are all expected to increase melting points.



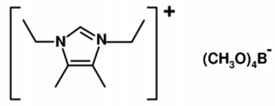
(I)



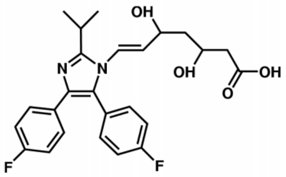
(II)



(III)



(IV)



(V)

The structure of the title compound, (I), contains tetrasubstituted imidazolium cations (Fig. 1) and Br^- anions, arranged in columns centered about the 2_1 screw axis at $(\frac{1}{2}, y, \frac{1}{2})$ (Fig. 2). Within a column, cations related by the 2_1 symmetry operation make a spiral arrangement along b. For each cation column, there are two bromide columns; in each of these, the anions are separated by the cell dimension b. There is little evidence of π-stacking, either within or between cation columns.

The phenyl and imidazolium rings are planar. Qualitatively, bond distances in the imidazolium ring show the typical short

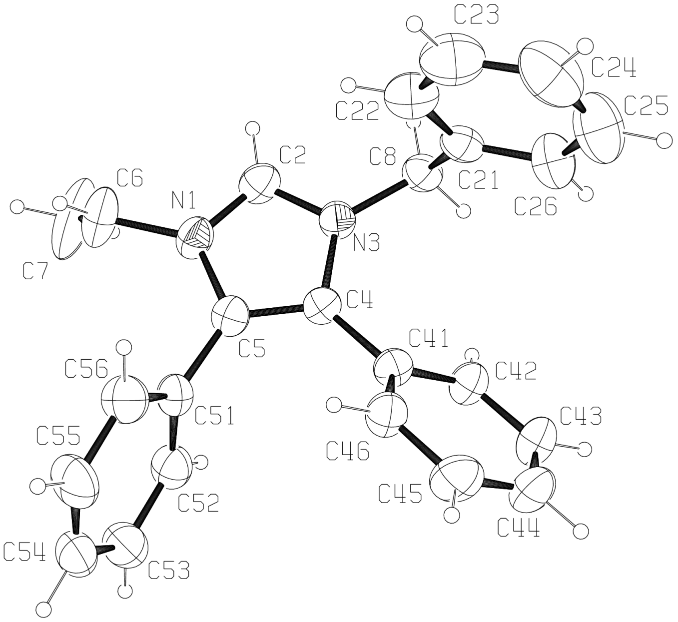


Figure 1
The structure of the cation of (I), showing 25% probability displacement ellipsoids.

(C2—N1 and C2—N3), long (N1—C5 and N3—C4), and short (C4—C5) variation (Elaiwi *et al.*, 1995). Quantitatively, they agree, within experimental error, with the averages of those reported for three other tetra-substituted imidazolium species, (II), (III) and (IV) (Kuhn *et al.*, 1996, 1999, 2001).

The α-vinyl and methylene C atoms (C6 and C8) lie in the imidazolium plane, with the attached phenyl (C21–C26) and methylene (C7) groups on opposite sides of the plane. The phenyl substituents at C4 and C5 are canted in the same direction and make angles of 46.8 (2) and 76.9 (2)°, respectively, with the imidazolium plane. Based on the im/vinyl (N1—C6—C7) dihedral angle of 74.1 (6)°, the π systems of the vinyl and imidazolium groups can interact only weakly. 1-Vinylimidazole and -imidazolium systems unhindered at the 2- and 5-positions have corresponding dihedral angles within approximately 10° of coplanarity, while the vinyl group in the tetra-substituted imidazole (V) (Chan *et al.*, 1993) is oriented similar to that in (I).

The above structural features yield a bulky low-symmetry cation, with the relatively unhindered atom C2 the most likely point for an anion to approach to minimize the Coulombic energy of the crystal. Consonant with this expectation, the shortest non-hydrogen inter-ionic contact is Br1···C2 at 3.568 (3) Å. Furthermore, the Br1···H2 distance (2.73 Å) and the C2—H2···Br1 angle (151°) suggest the presence of an inter-ionic hydrogen bond. The Br1···H2 distance is comparable to that reported (2.78 Å; Elaiwi *et al.*, 1995) for an *N,N′*-disubstituted imidazolium bromide, which was taken to indicate hydrogen bonding. The relatively high melting point of (I), 458 K, is consistent with relatively close contact between fairly localized charges and the presence of an interionic hydrogen bond.

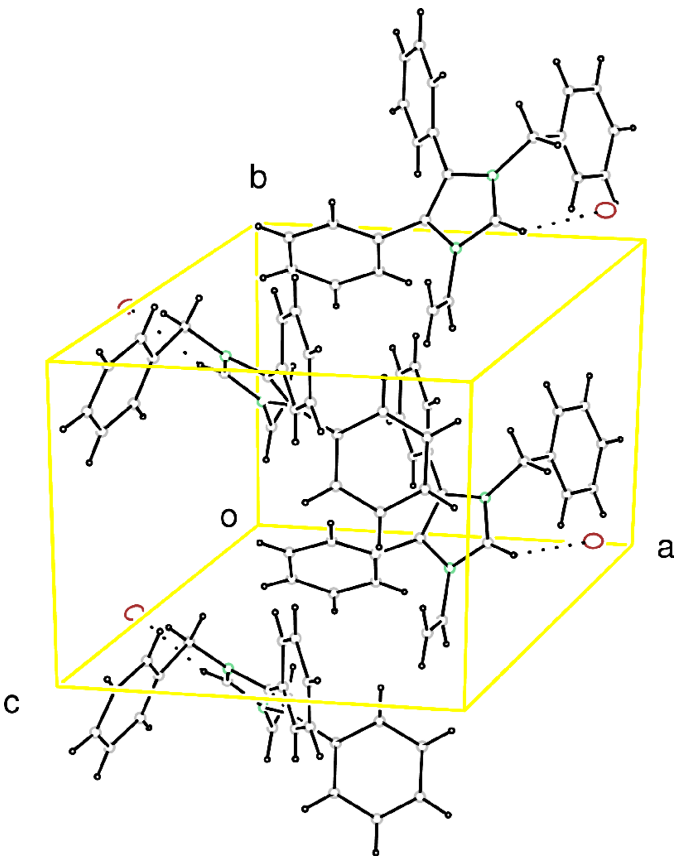


Figure 2
Unit-cell diagram, showing cation and anion columns stacked along the *b* axis.

Experimental

The title compound, (I), was obtained by the addition of an equimolar amount of benzyl bromide to a toluene solution of 1-ethyl-4,5-diphenylimidazole (Stibrany *et al.*, 2001) under atmospheric conditions. Crystals were grown by dissolving the precipitated product in acetonitrile and allowing slow evaporation. NMR spectroscopy of the reaction mixture showed that the expected product, 1-benzyl-3-ethyl-4,5-diphenylimidazolium bromide is formed first and then is rapidly oxidized to (I). The mechanism of this oxidation is currently under investigation.

Crystal data

$C_{24}H_{21}N_2^+\cdot Br^-$
$M_r = 417.34$
Monoclinic, $P2_1$
$a = 10.883$ (2) Å
$b = 9.440$ (2) Å
$c = 11.210$ (2) Å
$\beta = 111.07$ (1)°
$V = 1074.7$ (4) Å^3
$Z = 2$
$D_x = 1.296$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 705 reflections
$\theta = 3.9$–22.3°
$\mu = 1.92$ mm^{-1}
$T = 298$ (1) K
Rod, pale pink
0.52 × 0.26 × 0.20 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Blessing, 1995)
$T_{min} = 0.425$, $T_{max} = 0.681$
4474 measured reflections
3017 independent reflections
2259 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.0°$
$h = -12 \rightarrow 7$
$k = -11 \rightarrow 10$
$l = -12 \rightarrow 12$

Acta Cryst. (2002). E**58**, o848–o850 Robert T. Stibrany *et al.* • $C_{24}H_{21}N_2^+\cdot Br^-$ **o849**

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.106$
$S = 1.00$
3017 reflections
244 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.35$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}
Absolute structure: Flack (1983); 1196 Friedel pairs
Flack parameter = −0.016 (13)

Table 1
Selected geometric parameters (Å, °).

N3—C2	1.332 (6)	N1—C2	1.310 (6)
N3—C4	1.402 (5)	N1—C5	1.389 (6)
C4—C5	1.372 (6)		
C2—N3—C4	108.4 (4)	N1—C2—N3	110.1 (4)
C5—C4—N3	105.6 (4)	C4—C5—N1	107.5 (4)
C2—N1—C5	108.5 (4)		

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*-32 (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Bonhôte, P., Dias, A.-P., Papageorgiou, N., Kalyanasundaram, K. & Grätzel, M. (1996). *Inorg. Chem.* **35**, 1168–1178.

Bruker (2000). *SHELXTL* (Version 6.10), *SAINT* (Version 6.02) and *SMART* (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.

Burnett, M. N. & Johnson, C. K. (1996). *ORTEP*III. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.

Chan, C., Bailey, E. J., Hartley, C. D., Hayman, D. F., Hutson, J. L., Inglis, G. G. A., Jones, P. S., Keeling, S. E., Kirk, B. E., Lamont, R. B., Lester, M. G., Pritchard, J. M., Ross, B. C., Scicinski, J. J., Spooner, S. J., Smith, G., Steeples, I. P. & Watson, N. S. (1993). *J. Med. Chem.* **36**, 3646–3657.

Elaiwi, A., Hitchcock, P. B., Seddon, K. R., Srinivasan, N., Tan, Y.-M., Welton, T. & Zora, J. A. (1995). *J. Chem. Soc. Dalton Trans.* pp. 3467–3472.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Golding, J. J., MacFarlane, D. R., Spiccia, L., Forsyth, M., Skelton, B. W. & White, A. H. (1998). *Chem. Commun.* pp. 1593–1594.

Kuhn, N., Bohnen, H. & Henkel, G. (1996). *Z. Kristallogr.* **211**, 57.

Kuhn, N., Göhner, M., Steimann, M. & Nachtigal, Ch. (1999). *Z. Kristallogr. New Cryst. Struct.* **214**, 565–566.

Kuhn, N., Steimann, M. & Weyers, G. (2001). *Z. Kristallogr. New Cryst. Struct.* **216**, 315–317.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97-2. University of Göttingen, Germany.

Stibrany, R. T., Potenza, J. A., & Schugar, H. J. (2001). Private communication (reference number CCDC 172751) to the Cambridge Structural Database, 12 Union Road, Cambridge, England.

Welton, T. (1999). *Chem. Rev.* **99**, 2071–2083.

o850 Robert T. Stibrany *et al.* • $C_{24}H_{21}N_2^+ \cdot Br^-$ *Acta Cryst.* (2002). E**58**, o848–o850