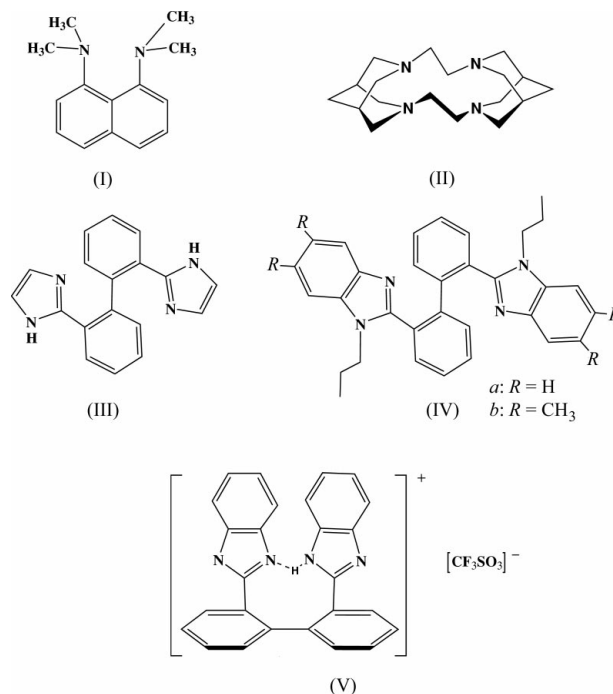


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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
Disorder in main residue
 R factor = 0.046
 wR factor = 0.146
Data-to-parameter ratio = 12.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>. $\kappa^2N^{13},N^{13'}$ -Hydro-*rac*-2,2'-bis[2-(1-propyl-
benzimidazol-2-yl)]biphenyl trifluoro-
methanesulfonate, the salt of a novel
proton spongeThe title salt, $\text{C}_{32}\text{H}_{31}\text{N}_4^+\cdot\text{CF}_3\text{SO}_3^-$, contains chains of
monoprotonated *rac*-2,2'-bis[2-(1-propylbenzimidazol-2-yl)]bi-
phenyl cations separated by trifluoromethanesulfonate anions.
The cations are linked by head-to-tail π -interactions of their
benzimidazole fragments. Protonation results in a strong
hydrogen bond involving the imine N atoms, which gives the
cations a tweezer or U shape.Received 15 August 2002
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Comment

Proton sponges, defined as species that exhibit high basicity
and low nucleophilicity, have been used as auxiliary bases in
organic synthesis (Llamas-Saiz *et al.*, 1994). Compound (I) is
considered to be the prototypical proton sponge, but others,
such as (II), are known (Miyahara *et al.*, 2001). Biphenyl-
based, basic bidentate ligands, such as (III) and (IV), with
three torsional degrees of freedom, have been used to enforce
tetrahedral coordination geometries for transition-metal
complexes in the +1 and +2 oxidation states (Knapp *et al.*,
1990; Xie *et al.*, 1999; Stibrany, 2001). We have observed that
benzimidazole biphenyl-based species of type (IV) can also
serve as proton sponges.

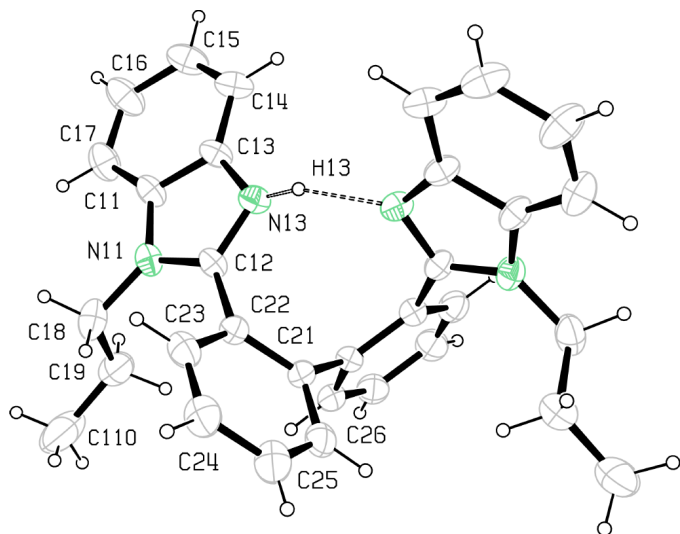


Figure 1
Molecular structure of the cation in (V), showing 25% probability displacement ellipsoids. For clarity, only one of the disordered atoms H13 is shown.

sulfonate anions arranged in layers perpendicular to *c* (Fig. 2), offset appropriately to be consistent with the body-centered lattice. Within a given layer, the cations form chains along *a*, in which individual centrosymmetrically related cations are linked head-to-tail by π -interactions of their benzimidazole fragments.

The cations are in sites $4e$ with site symmetry $2 (C_2)$, with the twofold axes passing through the midpoints of the C21—C21' and N13···N13' vectors. Consistent with this symmetry, H13 is disordered on two sites about the twofold axis. Both the benzimidazole (bz) and phenyl (ph) rings are planar, and they are canted with respect to each other by $64.60 (6)^\circ$ (bz/ph) and $88.60 (6)^\circ$ (ph/ph) to give the cation a U or tweezers shape. Metric parameters of the benzimidazole fragments agree well with those reported for neutral structures containing 2-phenylbenzimidazole groups (Bei *et al.*, 2000; Elerman & Kabak, 1997). In particular, the C12—N(imine) distance is shorter than the C12—N(amine) distance and both are shorter than the N—C11, C13 linkages. In (V) the near equality of C12—N distances found in imidazolium salts (Stibrany *et al.*, 2002a) is less apparent because the pair of benzimidazoles is mono-protonated.

The N13···N13' distance [$2.652 (2) \text{ \AA}$] is consistent with hydrogen bonding involving H13. In principle, this atom may be bonded either symmetrically or asymmetrically to the two imine N atoms. Both bonding modes were examined and better agreement with the data was obtained with H13 removed from the twofold axis to yield disordered, asymmetric hydrogen bonds. In protonated (I) [(IH⁺)] with different anions, both symmetric (X-ray diffraction, Woźniak *et al.*, 1990) and asymmetric (neutron diffraction, Woźniak *et al.*, 1996; Fox *et al.*, 2001) bonding has been reported. Recent structural (Pozharskii *et al.*, 2002; Fox *et al.*, 2001) and NMR (Perrin & Ohta, 2001; Pietrzak *et al.*, 2001) studies of proton

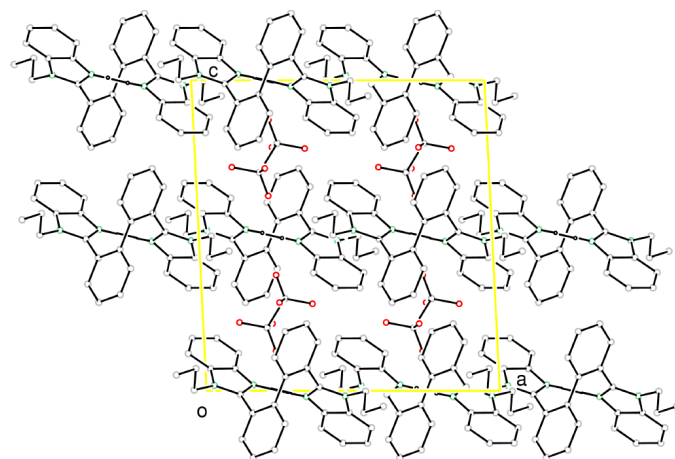


Figure 2
Unit-cell (010) projection, showing cation chains along the *a* axis and the disordered protons H13. Other H atoms have been omitted for clarity.

sponges suggest that asymmetric bonding with a shallow double-minimum potential well is the norm. We conclude that, in the present system, H13 is disordered over two sites about the twofold axis and that placing it on the twofold axis, which would result in an unusually large N13—H13 distance (1.34 \AA), would be an artifact of the refinement.

For H13, the shortest interionic contact is to H16 of an adjacent cation (3.82 \AA), indicating that the hydrogen-bonded proton is encapsulated within the cation and that the center of positive charge is relatively far removed from other species, including the trifluoromethanesulfonate anions. To estimate the base strength of (IVa) and (IVb), competitive NMR experiments were performed. In deuterated acetonitrile, (IVb) deprotonates (IH⁺) while (IVa) does not, suggesting that, in this solvent, (IV) and (I) have comparable pK_a values (Stibrany *et al.*, 2002b).

Experimental

The title salt, (V), was obtained by the addition of an equimolar amount of a $2.57 M$ solution of triflic acid in methanol to an acetonitrile solution of *rac*-2,2'-bis[2-(1-propylbenzimidazol-2-yl)]biphenyl. Crystals were obtained by slow vapor diffusion of diethyl ether. ¹H NMR (400 MHz, CDCl₃): $\delta = 16.03 (br s, 1H)$, $7.67 (d, J = 7.5 \text{ Hz}, 2H)$, $7.48 (m, 12H)$, $7.21 (d, J = 6.0 \text{ Hz}, 2H)$, $4.40 (m, 4H)$, $1.90 (m, 4H)$, $0.97 (t, J = 7.2 \text{ Hz}, 6H)$. ¹³C NMR (400 MHz, CDCl₃): $\delta = 150.6$, 140.3 , 135.1 , 133.1 , 131.6 , 130.4 , 130.3 , 129.3 , 125.4 , 125.3 , 125.0 , 116.5 , 112.3 , 46.9 , 23.2 , 11.3 . ¹⁹F NMR (400 MHz, CDCl₃): $\delta = -78.6$.

Crystal data

C₃₂H₃₁N₄⁺·CF₃O₃S⁻
 $M_r = 620.69$
 Monoclinic, $I2/a$
 $a = 14.383 (3) \text{ \AA}$
 $b = 14.217 (3) \text{ \AA}$
 $c = 15.252 (5) \text{ \AA}$
 $\beta = 92.85 (1)^\circ$
 $V = 3115.1 (14) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.323 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 903 reflections
 $\theta = 4.0\text{--}23.6^\circ$
 $\mu = 0.16 \text{ mm}^{-1}$
 $T = 298 (1) \text{ K}$
 Plate, colorless
 $0.50 \times 0.25 \times 0.18 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer 2479 independent reflections
 1925 reflections with $I > 2\sigma(I)$
 φ and ω scans $R_{\text{int}} = 0.017$
 Absorption correction: multi-scan (*SADABS*; Blessing, 1995) $\theta_{\text{max}} = 25.0^\circ$
 $T_{\text{min}} = 0.953$, $T_{\text{max}} = 0.971$ $h = -16 \rightarrow 16$
 6104 measured reflections $k = -16 \rightarrow 15$
 $l = -17 \rightarrow 14$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.091P)^2 + 0.8886P]$
 $R[F^2 > 2\sigma(F^2)] = 0.046$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.146$ $(\Delta/\sigma)_{\text{max}} < 0.001$
 $S = 1.00$ $\Delta\rho_{\text{max}} = 0.16 \text{ e } \text{\AA}^{-3}$
 2479 reflections $\Delta\rho_{\text{min}} = -0.31 \text{ e } \text{\AA}^{-3}$
 200 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (\AA , $^\circ$).

N13—C12	1.320 (2)	N11—C11	1.392 (3)
N13—C13	1.387 (2)	C11—C13	1.387 (3)
N11—C12	1.351 (2)		
C12—N13—C13	107.47 (16)	N13—C12—N11	111.23 (16)
C12—N11—C11	107.06 (16)	N13—C13—C11	107.70 (17)
C13—C11—N11	106.54 (16)		

The structure was originally refined in space group $C2/c$ with $\beta = 131.81 (1)^\circ$; the space group was converted to $I2/a$ with $\beta = 92.85 (1)^\circ$ to reduce correlation among x - and z -related parameters. The trifluoromethanesulfonate anions adopt the staggered-ethane conformation and are disordered centrosymmetrically about the 4c sites, such that the CF_3^- and SO_3^- fragments, which have approximately the same size and shape, overlap to a large extent. Attempts to refine the atoms of these fragments individually resulted in large correlation coefficients (some greater than 0.95) and unrealistic parameters. Consequently, the anion was refined as a centrosymmetric pair of four-atom fragments (50% C and S in one position, 50% O and F in the remaining three positions); this refinement gave acceptable correlation coefficients and better agreement with the data than unconstrained or restrained refinements. Refinement in space group Ia was attempted, but did not remove the hydrogen or anion disor-

ders. However, as expected, parameter s.u. values were substantially larger in Ia than in $I2/a$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3* (Burnett & Johnson, 1996) and *ORTEP32* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

References

Bei, F., Jian, F., Yang, X., Lu, L., Wang, X., Raj, S. S. S. & Fun, H.-K. (2000). *Acta Cryst.* **C56**, 718–719.
 Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
 Bruker (2000). *SHELXTL* (Version 6.10), *SAINTE-Plus* (Version 6.02) and *SMART-WNT2000* (Version 5.622). Bruker AXS Inc., Madison, Wisconsin, USA.
 Burnett, M. N. & Johnson, C. K. (1996). *ORTEP3* Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
 Elerman, Y. & Kabak, M. (1997). *Acta Cryst.* **C53**, 372–374.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Fox, M. A., Goeta, A. E., Howard, J. A. K., Hughes, A. K., Johnson, A. L., Keen, D. A., Wade, K. & Wilson, C. C. (2001). *Inorg. Chem.* **40**, 173–175.
 Knapp, S., Keenan, T. P., Zhang, X., Fikar, R., Potenza, J. A. & Schugar, H. J. (1990). *J. Am. Chem. Soc.* **112**, 3452–3464.
 Llamas-Saiz, A. L., Foces-Foces, C. & Elguero, J. (1994). *J. Mol. Struct.* **328**, 297–323.
 Miyahara, Y., Goto, K. & Inazu, T. (2001). *Tetrahedron Lett.* **42**, 3097–3099.
 Perrin, C. L. & Ohta, B. K. (2001). *J. Am. Chem. Soc.* **123**, 6520–6526.
 Pietrzak, M., Wehling, J., Limbach, H.-H., Golubev, N. S., López, C., Caramunt, R. M. & Elguero, J. (2001). *J. Am. Chem. Soc.* **123**, 4338–4339.
 Pozharskii, A. F., Ozeryanskii, V. A. & Starikova, Z. A. (2002). *J. Chem. Soc. Perkin Trans. 2*, pp. 318–322.
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
 Stibrany, R. T. (2001). US Patent 6,180,788.
 Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2002a). *Acta Cryst.* **E58**, o848–o850.
 Stibrany, R. T., Schugar, H. J. & Potenza, J. A. (2002b). To be published.
 Woźniak, K., Krygowski, T. M., Kariuki, B., Jones, W. & Grech, E. (1990). *J. Mol. Struct.* **240**, 111–118.
 Woźniak, K., Wilson, C. C., Knight, K. S., Jones, W. & Grech, E. (1996). *Acta Cryst.* **B52**, 691–696.
 Xie, B., Elder, T., Wilson, L. J. & Stanbury, D. M. (1999). *Inorg. Chem.* **38**, 12–19.