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# Zwitterionic 5-(1-piperidiniomethyl)-1*H*-tetrazolide

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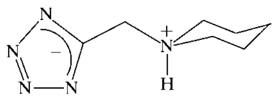
The title compound, $C_7H_{13}N_5$, a tetrazole analogue of betaines, exists as a zwitterion, with the H atom of the tetrazole ring being transferred to the piperidine ring N atom. The tetrazole ring symmetry is close to $C_{2v}$, which suggests strong charge delocalization in the N—C—N fragment of the ring. There are classical hydrogen bonds in the structure which are responsible for the formation of two-membered aggregates.

## Comment

Tetrazole and its 5-substituted derivatives have attracted research interest in the fields of bioorganic and medicinal chemistry, due to the isosterity and acidity of the *N*-unsubstituted tetrazole ring being comparable with those of the carboxylic acid group (Butler, 1996). 5-Monosubstituted tetrazoles with an aminomethyl substituent represent an interesting class of tetrazole analogues of $\alpha$-amino acids. One should expect that such compounds may exist in the form of a zwitterion. In this paper, we report the molecular and crystal structures of the title compound, (I) (Fig. 1). No crystal data were found for 5-($\alpha$-aminomethyl)tetrazoles (Cambridge Structural Database, Version 5.23 of September 2002; Allen, 2002).



(I)

As expected, compound (I) exists as a zwitterion, with the H atom of the tetrazole ring being transferred to the piperidine ring N atom. The main geometrical features of (I) are given in Table 1.

As can be seen from Table 1, the tetrazole ring in (I) is rather symmetrical. The C5—N1 and C5—N4 bond lengths are practically the same, and the N1—N2 bond length is the same as that for N3—N4. The N2—N3 bond is the shortest in the ring. This bond symmetry is supported by angle symmetry (Table 1). Moreover, the tetrazole ring is essentially planar, to within 0.0019 (6) Å. Thus, the ring symmetry is close to $C_{2v}$. Taking into account the essential difference between the C5—N1 and C5—N4 bond lengths in 5-substituted tetrazoles, one can conclude that there is strong charge delocalization in the N1—C5—N4 fragment of (I).

The protonation at atom N7 leads to an increase in the N7—C distances and to the angles at N7 being close to tetrahedral (Table 1). The piperidine ring adopts a chair conformation, with the H atom at N7 in the axial position, whereas the bulky tetrazole substituent is located in the equatorial position.

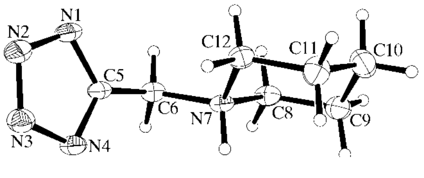


**Figure 1**
A view of the molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

Inspection of the packing structure of (I) reveals classical N7—H7···N4 hydrogen bonds (Table 2). These are responsible for the formation of two-membered aggregates (Fig. 2), additionally stabilized by weak C9—H9*B*···N3 interactions (Table 2). Only non-classical hydrogen bonds (Table 2), together with van der Waals interactions, exist between these aggregates in the structure of (I).

It should be noted that the title compound is only the second structurally characterized tetrazole analogue of betaines after 5-(2′-dimethylaminoethyl)tetrazole (Chertanova *et al.*, 1988). The main features of the tetrazole ring geometry of the latter compound are close to those found for (I).

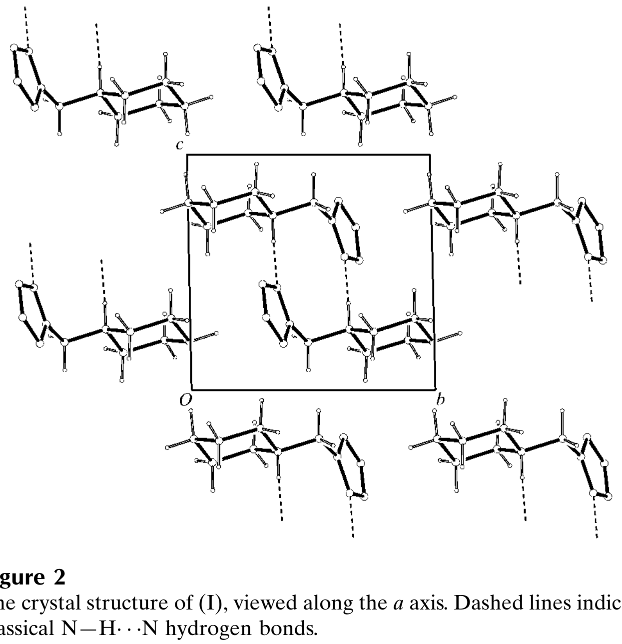


**Figure 2**
The crystal structure of (I), viewed along the *a* axis. Dashed lines indicate classical N—H···N hydrogen bonds.

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## Experimental

The title compound was synthesized by the aminomethylation of tetrazole with piperidine and formaldehyde, according to the method of Karavai & Gaponik (1991). The compound decomposes at 528 K. Single crystals of (I) were grown by slow evaporation in air of an ethanol solution. Spectroscopic analysis, $^1$H NMR [100 MHz, $(CD_3)_2SO$]: $\delta$ 1.30–1.82 (*m*, 6H, 3 × $CH_2$), 3.00 (*t*, 4H, 2 × $CH_2$), 4.25 (*s*, 2H, $CH_2$).

### *Crystal data*

$C_7H_{13}N_5$
$M_r$ = 167.22
Triclinic, $P\overline{1}$
$a$ = 6.1664 (10) Å
$b$ = 8.3913 (18) Å
$c$ = 8.6842 (17) Å
$\alpha$ = 90.062 (17)°
$\beta$ = 110.351 (15)°
$\gamma$ = 93.176 (16)°
$V$ = 420.56 (14) Å$^3$

$Z$ = 2
$D_x$ = 1.321 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta$ = 20.4–23.3°
$\mu$ = 0.09 mm$^{-1}$
$T$ = 293 (2) K
Prism, colourless
0.50 × 0.40 × 0.38 mm

### *Data collection*

Nicolet *R*3*m* four-circle diffractometer
$\omega/2\theta$ scans
2761 measured reflections
2467 independent reflections
2118 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.018

$\theta_{\rm max}$ = 30°
$h = 0 \rightarrow 8$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 11$
3 standard reflections every 100 reflections intensity decay: 1.7%

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.118$
$S$ = 1.06
2467 reflections
161 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0690P)^2 + 0.0378P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 0.17 e Å$^{-3}$
$\Delta\rho_{\rm min}$ = −0.26 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| N1—C5 | 1.3313 (11) | N4—C5 | 1.3293 (11) |
| N1—N2 | 1.3480 (13) | C6—N7 | 1.5058 (12) |
| N2—N3 | 1.3062 (12) | N7—C12 | 1.5003 (11) |
| N3—N4 | 1.3489 (11) | N7—C8 | 1.5048 (11) |
| | | | |
| C5—N1—N2 | 104.73 (7) | N4—C5—C6 | 125.48 (7) |
| N3—N2—N1 | 109.69 (8) | N1—C5—C6 | 123.06 (7) |
| N2—N3—N4 | 108.96 (8) | C12—N7—C8 | 111.25 (7) |
| C5—N4—N3 | 105.17 (7) | C12—N7—C6 | 112.71 (7) |
| N4—C5—N1 | 111.45 (8) | C8—N7—C6 | 109.07 (7) |

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N7—H7···N4$^{\rm i}$ | 0.943 (14) | 1.874 (14) | 2.8007 (11) | 166.9 (11) |
| C6—H6*A*···N2$^{\rm ii}$ | 0.979 (13) | 2.482 (13) | 3.4555 (13) | 172.9 (10) |
| C8—H8*A*···N1$^{\rm iv}$ | 1.004 (13) | 2.602 (13) | 3.5345 (13) | 154.5 (9) |
| C9—H9*B*···N3$^{\rm i}$ | 0.975 (14) | 2.608 (13) | 3.4067 (15) | 139.3 (10) |
| C12—H12*B*···N3$^{\rm iii}$ | 0.975 (12) | 2.579 (12) | 3.4801 (14) | 153.7 (9) |

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

H-atom positions were located in a difference Fourier map and all associated parameters were refined freely. Refined C—H distances were in the range 0.95 (2)–1.01 (2) Å.

Data collection: *R*3*m Software* (Nicolet, 1980); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1125). Services for accessing these data are described at the back of the journal.

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