

## Hydrogen bonding in 2-phenylimidazoline

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

Department of Chemistry and Chemical Biology,  
Rutgers, The State University of New Jersey, 610  
Taylor Road, Piscataway, New Jersey 08854-  
8087, USACorrespondence e-mail:  
potenza@rutchem.rutgers.edu

## Key indicators

Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.051  
 $wR$  factor = 0.158  
Data-to-parameter ratio = 11.4For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_9\text{H}_{10}\text{N}_2$ , crystallizes with two formula units in the asymmetric unit. When viewed along the  $b$  axis, the two crystallographically unique molecules form alternating columns along  $a$ . Within each column, the molecules are linked by  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds to form infinite chains. Intermolecular  $\text{C}\cdots\text{C}$  and  $\text{C}\cdots\text{N}$  distances suggest that molecules in adjacent columns are linked primarily by  $\text{C}-\text{H}\cdots\pi$  interactions, with little, if any,  $\pi$  stacking. Metric parameters for the imidazoline fragments are comparable to those of other 2-substituted imidazoline species.

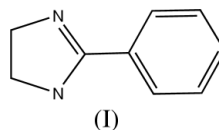
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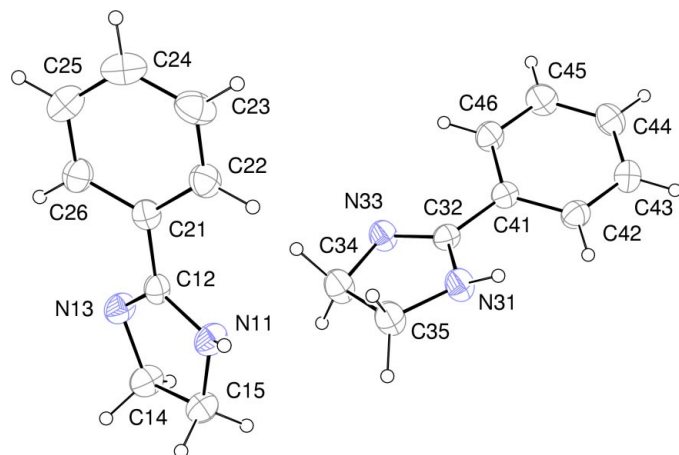
## Comment

Our continuing interest in imidazole and benzimidazole chemistry has led us to prepare a variety of species containing these units, including ionic salts (Stibrany, Potenza & Schugar, 2002), catalysts (Patil *et al.*, 2003; Stibrany *et al.*, 2003; Stibrany, Matturo *et al.*, 2002), geometrically constraining ligands (Knapp *et al.*, 1990; Stibrany *et al.*, 2004) and proton sponges (Stibrany, Schugar & Potenza, 2002). We have also been interested in improved methods for the oxidation of imidazolines to imidazoles (Hughey *et al.*, 1980). The title compound, (I),  $\text{C}_9\text{H}_{10}\text{N}_2$ , whose structure we report here, is the result of a more facile preparation of imidazolines, which we intend to use in future oxidation studies.



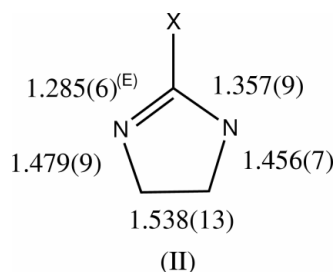
The structure of (I) contains two 2-phenylimidazoline molecules in the asymmetric unit (Fig. 1). Both phenyl rings are effectively planar, with r.m.s. deviations from planarity of 0.004 and 0.006 Å. In contrast, the imidazoline fragments exhibit substantially larger r.m.s. deviations from planarity (0.025 and 0.043 Å), suggesting a slight puckering of the five-membered rings. In each molecule, the phenyl ( $\varphi$ ) and imidazoline (im) units are twisted with respect to each other to approximately the same degree, as indicated by the  $\varphi/\text{im}$  dihedral angles of 24.6 (1) and 22.2 (1)° for the two unique molecules. Corresponding bond distances and angles for the two molecules exhibit r.m.s. fits of 0.008 Å and 0.36°, demonstrating the degree to which the two molecules are similar. Despite these similarities, the molecules do not appear to be related either by crystallographic or non-crystallographic symmetry.

Bond distances in the imidazoline fragments (Table 1) show the typical long (N11—C12 and N31—C32) and short (N13—

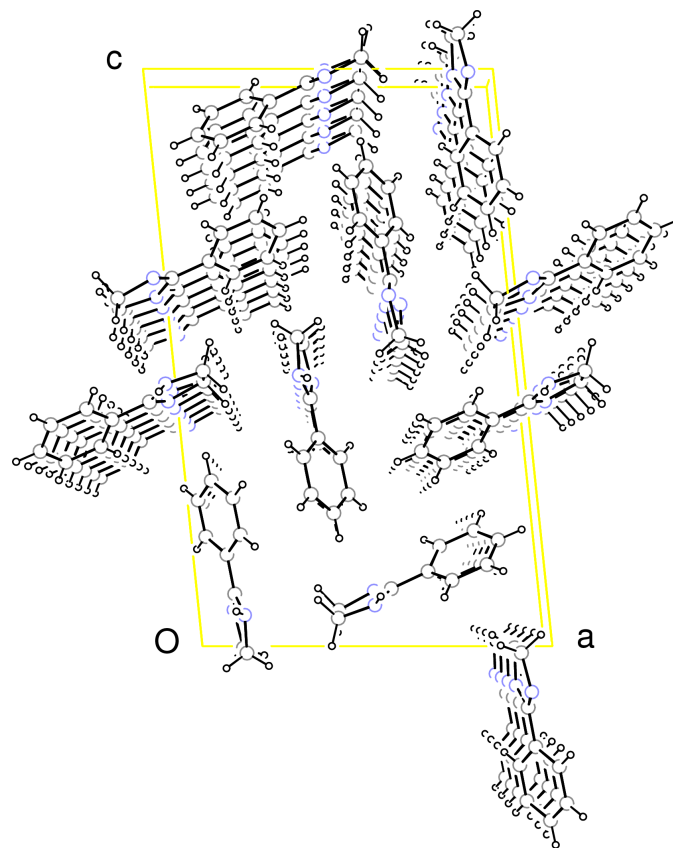


**Figure 1**  
The contents of the asymmetric unit, showing 30% probability displacement ellipsoids and the atom-numbering scheme.

C12 and N33–C32) variation characteristic of  $N_{\text{amine}}\text{—C}$  and  $N_{\text{imine}}\text{—C}$  bonds, respectively. Furthermore, the C14–C15 and C34–C35 lengths are fully consistent with  $Csp^3\text{—}Csp^3$  linkages. To within experimental error, corresponding distances in the imidazoline rings of (I) are equal to the averages, shown in (II), of those reported in the Cambridge Structural Database (Version 5.24; Allen, 2002) for six structures containing 2-substituted imidazoline fragments [refcodes BEQWEZ (Brennan & McKee, 1999), IBEVEQ (Baron *et al.*, 1999), LOFEXD10 (Cary *et al.*, 1980), XIGCEV (Saczewski *et al.*, 2001), DEBTUZ (Tilley *et al.*, 1985) and TUDSEQ (Parvez, 1997)]. The  $\varphi$ /im twist angles, coupled with the clearly differentiated  $N_{\text{imine}}\text{—C}$  and  $N_{\text{amine}}\text{—C}$  bonds, ensure that each molecule is axially chiral, while the glide-plane and inversion-symmetry operations of the space group demand equal amounts of each enantiomer. As a result, the crystal is technically an equimolar racemic mixture of two slightly different pairs of enantiomers.



In the crystal structure (Fig. 2), the molecules form columns along the  $b$  axis. Within a given column, individual molecules are related to each other by translation and are therefore of a given type; they are linked by strong two-center  $N\text{—H}\cdots N(x, y - 1, z)$  hydrogen bonds (Table 2) and form infinite chains along the  $b$  axis (Fig. 3). Columns of a given type form alternating layers parallel to the  $(10\bar{1})$  planes which contain the direction of the translational component of the  $n$ -glide plane; in this view, the structure appears as a slipped-herringbone



**Figure 2**  
A view of the structure along the  $b$  axis.

pattern. Intermolecular  $C\cdots C$  and  $C\cdots N$  distances indicate that molecules in adjacent columns are linked primarily by  $C\text{—}H\cdots\pi$  interactions, with little, if any,  $\pi\text{—}\pi$  bonding.

## Experimental

A published procedure for the facile preparation of imidazolines was used to prepare 2-phenylimidazoline (Kawasaki & Hachiya, 1973). In this procedure, 1.05 molar equivalents of ethylenediamine per equivalent of benzonitrile were heated in the presence of cysteine hydrochloride (1 mol%) at 373 K until the cessation of ammonia evolution was observed. Upon recrystallization from 2-propanol, crystals of (I) were obtained in greater than 90% yield.

### Crystal data

$C_9H_{10}N_2$	$D_x = 1.243 \text{ Mg m}^{-3}$
$M_r = 146.19$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 911 reflections
$a = 13.4996(6) \text{ \AA}$	$\theta = 3.7\text{--}22.0^\circ$
$b = 5.1922(2) \text{ \AA}$	$\mu = 0.08 \text{ mm}^{-1}$
$c = 22.4019(13) \text{ \AA}$	$T = 295(2) \text{ K}$
$\beta = 95.880(4)^\circ$	Block, colorless
$V = 1561.95(13) \text{ \AA}^3$	$0.36 \times 0.22 \times 0.12 \text{ mm}$
$Z = 8$	

### Data collection

Bruker SMART CCD area-detector diffractometer	2714 independent reflections
$\varphi$ and $\omega$ scans	1894 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$R_{\text{int}} = 0.037$
$T_{\text{min}} = 0.876, T_{\text{max}} = 1.00$	$\theta_{\text{max}} = 25.0^\circ$
11 084 measured reflections	$h = -16 \rightarrow 16$
	$k = -6 \rightarrow 6$
	$l = -26 \rightarrow 26$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.158$   
 $S = 1.00$   
 2714 reflections  
 239 parameters  
 H atoms treated by a mixture of  
 independent and constrained  
 refinement

$$w = 1/[\sigma^2(F_o^2) + (0.086P)^2 + 0.4484P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{\AA}^{-3}$

Table 1

Selected interatomic distances (Å).

N11—C12	1.362 (3)	N31—C32	1.361 (3)
N13—C12	1.285 (3)	N33—C32	1.280 (3)
N11—C15	1.454 (3)	N31—C35	1.454 (3)
N13—C14	1.467 (3)	N33—C34	1.482 (3)
C14—C15	1.534 (4)	C34—C35	1.537 (4)

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N11—H11 $\cdots$ N13 <sup>i</sup>	0.87 (4)	2.20 (4)	3.037 (3)	163 (3)
N31—H31 $\cdots$ N33 <sup>i</sup>	0.91 (3)	2.19 (3)	3.046 (3)	157 (2)

Symmetry code: (i)  $x, y - 1, z$ .

H atoms of the imidazoline fragments were refined isotropically. For the phenyl groups, H atoms were positioned geometrically and treated as riding, with  $Csp^2-H$  distances set to 0.93 Å and displacement parameters set at  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-32* (Farrugia, 1997); software used to prepare material for publication: *SHELXTL* (Bruker, 2000).

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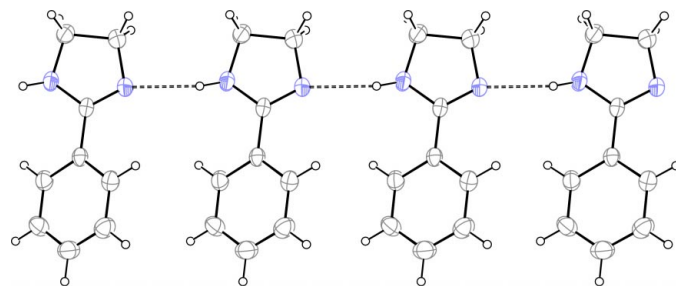


Figure 3

Partial view, normal to (100), of one of the infinite chains of hydrogen-bonded molecules of (I). N11—H11 $\cdots$ N13( $x, y - 1, z$ ) hydrogen bonds are shown as dashed lines.

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