# 5-Phenyl-3,4-dihydro-2H-pyrrole: the first example of a planar mono-substituted 1-pyrroline

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In the title compound, $C_{10}H_{11}N$, the molecules assemble as pseudo-dimers through $\pi$–$\pi$ interactions, each dimer being rotated by about 90° with respect to its neighbours. The relative positioning of the dimers and C—H$\cdots\pi$ interactions give, when seen along $a$, a supramolecular zigzag arrangement. The compound contains a planar pyrroline ring and, as a whole, its molecular conformation is also planar, which represents the first example of a totally planar 2-substituted 1-pyrroline and the simplest ever reported by X-ray diffraction.

## Comment

Pyrrole and its derivatives, (II), are widely known five-membered heterocyclic compounds. Due to their broad range of applications in areas such as natural products, bioactive molecules, pharmaceuticals, anion-binding systems, *etc.*, many efforts have been made to develop new synthetic routes for this type of compound (Rao & Jothilingam, 2001; Braun *et al.*, 2001; Hewton *et al.*, 2002; Sessler *et al.*, 2005).
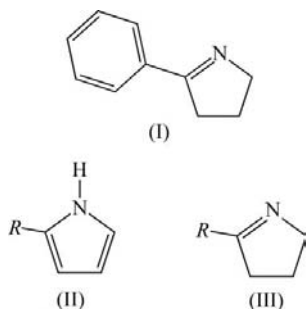
2-Substituted 1-pyrrolines, (III), also called 3,4-dihydro-2H-pyrroles, are important compounds as well, since they can exhibit strong flavouring and odorant properties, such as a cooked-rice flavour (Harrison & Dake, 2005; Fuganti *et al.*, 2007), besides antiviral (Moriarty *et al.*, 2006) or antifungal activity (Verniest *et al.*, 2005). They can also be found as

structural motifs in bioactive molecules, such as alkaloids (Usubillaga *et al.*, 1982), or can be used as optically active tryptophan analogues (van Esseveldt *et al.*, 2003). Recently, our group reported the aromatization of 2-phenyl-1-pyrroline to 2-phenylpyrrole using activated carbon as the dehydrogenation agent under mild reaction conditions (Carabineiro *et al.*, 2006). In this context, the preparation of 2-phenyl-1-pyrroline was carried out using an adaptation of a synthetic procedure previously reported in the literature (Craig *et al.*, 1931). In this work, we report the crystal structure of the title compound, namely 5-phenyl-3,4-dihydro-2H-pyrrole (or 2-phenyl-1-pyrroline), (I), which, to the best of our knowledge, is the first example of a wholly planar monosubstituted 1-pyrroline determined by single-crystal X-ray diffraction. The molecular structure of this compound is shown in Fig. 1.

The geometry and conformation of pyrroline rings have been subjects of great interest. Theoretical calculations (Boggs & Kim, 1985) and experimental gas-phase microwave and IR spectroscopy measurements (Edwards *et al.*, 1985) on unsubstituted 1-pyrroline have shown that the ring deviates only slightly from planarity (Edwards *et al.*, 1985). However, in the solid state, the pyrroline ring generally exists in an envelope conformation with a C atom deviating significantly from the mean plane of the remaining four atoms of the heterocycle (Steel *et al.*, 1992). Nevertheless, the title compound, (I), despite having a phenyl substituent at the iminic position (C1), shows a planar conformation, where the highest deviation is shown by atom C3 which is only 0.0258 (6) Å from the average plane of the pyrroline ring. The geometry of the entire structure is also nearly planar, since the dihedral angle between the two rings is only 3.34 (10)°.

The sum of the internal angles of the heterocycle is 539.83 (9)°, a value that is very close to that of a regular planar pentagon (540°). The iminic bond length is 1.2771 (12) Å and all the other bonds in the heterocycle have lengths that correspond to typical values for single C—C and C—N bonds (Allen *et al.*, 1987). Consequently, the internal angles of the heterocycle are much lower than those defined by the corresponding $Nsp^2$, $Csp^2$ and $Csp^3$ atoms, which is consistent with a considerable amount of ring strain and also with a certain amount of conjugation of the C=N group with the phenyl ring.

A great variety of geometries and conformations is found in different derivatives of 1-pyrroline, depending on the positions and relative orientations of the substituents. The second scheme (below) shows some examples of the simplest
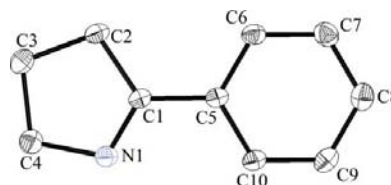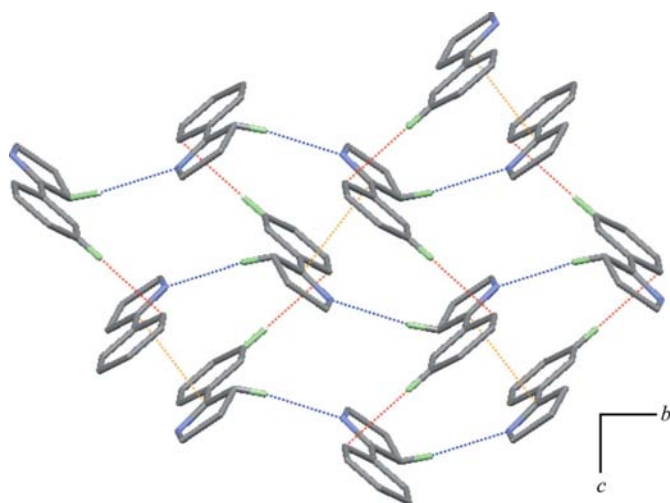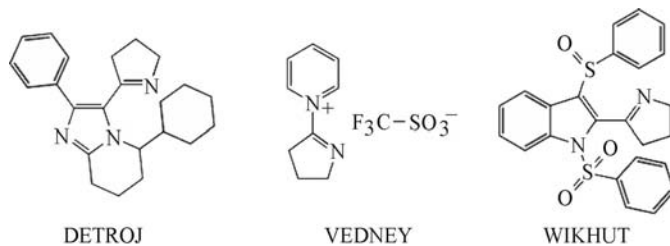
**Figure 1**
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.
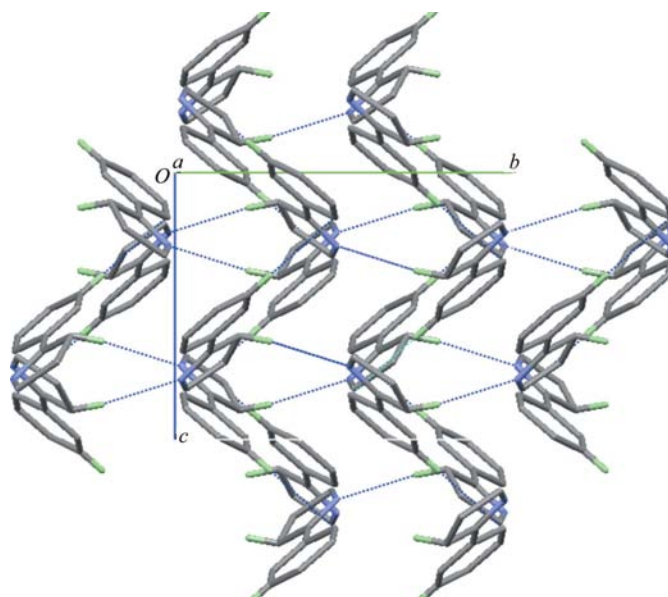
# organic compounds



**Figure 2**
A view of the pseudo-dimers observed in the crystal structure of (I), rotated relative to each other by about 90°. Dashed lines represent C—H···N, C—H···π and π–π interactions (blue, red and orange, respectively, in the electronic version of the paper).



**Figure 3**
The packing of the crystal structure of (I), viewed along the *a* axis.

2-substituted 1-pyrrolines found in the Cambridge Structural Database (CSD, Version 5.29; Allen, 2002) with refcodes DETROJ (Fuhrer *et al.*, 1985), VEDNEY (Charette *et al.*, 2005) and WIKHUT (Beddoes *et al.*, 1994). A brief analysis of some of the structural parameters of these compounds (such as the sum of the internal angles, the deviation from planarity, torsion angles, and the angle between the plane that contains the pyrroline ring and that of the 2-substituent) allows their comparison with the title compound, (I). For DETROJ, VEDNEY and WIKHUT, the sums of the internal angles are 537.36, 539.52/536.02 (molecules 1 and 2), and 539.32°, respectively. For all structures, atom C3 deviates most from the average plane of the pyrroline, by 0.086 Å in DETROJ, 0.042/0.123 Å in VEDNEY (molecules 1 and 2) and 0.049 Å in WIKHUT. For DETROJ and VEDNEY, the geometry of the entire structure is not planar, since the angles between the planes of pyrroline and its 2-substituent are 21.38 and 11.51/24.91° (molecules 1 and 2), respectively. In fact, WIKHUT has a truly perpendicular geometry, with an angle between the



DETROJ            VEDNEY            WIKHUT

planes of 89.62°. The difference in geometry is further enhanced by comparing the corresponding torsion angles, presented in Table 1. A comparison of these structures with that of (I) leads readily to the conclusion that the present 2-phenyl-1-pyrroline is the first example of a totally planar 2-substituted 1-pyrroline and the simplest ever reported by X-ray diffraction.

No classical hydrogen-bond synthons are found in the molecule of (I), but it is possible to observe the existence of weak intermolecular C—H···N and C—H···π interactions that explain the packing found in the crystal structure. Each pyrroline shows four short contacts with four different neighbouring molecules: two bonds of the type C2—H2B···N1 [C2···N1 = 3.594 (1) Å, H2B···N1 = 2.63 Å and C2—H2B···N1 = 172°; symmetry code: (i) $1 - x, y + \frac{1}{2}, -z + \frac{3}{2}$] and two of the type C7—H7···π(C10) [C7···π(C10) = 3.678 (1) Å, H7···π(C10) = 2.89 Å and C7—H7···π(C10) = 143°; symmetry code: (ii) $x, \frac{1}{2} - y, z + \frac{1}{2}$]. These interactions enable the formation of pseudo-dimers exhibiting π–π interactions [π(C1)···π(C1) = 3.636 (1) Å; symmetry code: (iii) $1 - x, -y, 2 - z$], as shown in Fig. 2, where the corresponding molecules are antiparallel to each other.

Due to the supramolecular interactions described above, the crystal packing shows a zigzag arrangement when viewed along *a*, as depicted in Fig. 3.

## Experimental

Diethyl ether, xylene and bromobenzene were predried over activated 4 Å molecular sieves and then distilled from sodium and kept under a nitrogen atmosphere. The synthetic procedure followed for the synthesis of 2-phenyl-1-pyrroline was that used previously by our group (Carabineiro *et al.*, 2006) and was adapted from the literature (Craig *et al.*, 1931). After trap-to-trap vacuum distillation, colourless crystals of (I) were grown from a solution in a mixture of xylene and pyrroline (molar ratio 1:16) at 273 K.

*Crystal data*

| | |
|---|---|
| $C_{10}H_{11}N$ | $V = 1572.8 (4)$ Å$^3$ |
| $M_r = 145.20$ | $Z = 8$ |
| Orthorhombic, *Pbca* | Mo $K\alpha$ radiation |
| $a = 18.326 (3)$ Å | $\mu = 0.07$ mm$^{-1}$ |
| $b = 10.3875 (14)$ Å | $T = 150 (2)$ K |
| $c = 8.2618 (12)$ Å | $0.37 \times 0.30 \times 0.30$ mm |

**Table 1**
Comparison of torsion angles in (I), DETROJ, VEDNEY and WIKHUT (°).

The nomenclature used for the torsion angles is that of compound (I); all torsion angles for the other compounds are the corresponding ones.

| | Compound (I) | DETROJ[a] | VEDNEY[b] Molecule 1 | VEDNEY Molecule 2 | WIKHUT[c] |
|---|---|---|---|---|---|
| N1—C1—C5—C6 | −176.40 (9) | 175.89 | −168.29 | −153.65 | −93.33 |
| C2—C1—C5—C10 | −176.52 (8) | −162.19 | 170.63 | −152.11 | −91.63 |
| N1—C1—C5—C10 | 3.05 (13) | −0.68 | 10.46 | 24.57 | 84.51 |
| C2—C1—C5—C6 | 4.03 (13) | 14.38 | 10.61 | 29.67 | 90.82 |

References: (a) Fuhrer *et al.* (1985); (b) Charette *et al.* (2005); (c) Beddoes *et al.* (1994).

### Data collection

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 46880 measured reflections |
| Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) | 2247 independent reflections |
| | 1856 reflections with $I > 2\sigma(I)$ |
| $T_{min} = 0.883$, $T_{max} = 0.979$ | $R_{int} = 0.051$ |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)] = 0.042$ | 100 parameters |
| $wR(F^2) = 0.120$ | H-atom parameters constrained |
| $S = 1.07$ | $\Delta\rho_{max} = 0.29$ e Å$^{-3}$ |
| 2247 reflections | $\Delta\rho_{min} = -0.19$ e Å$^{-3}$ |

All H atoms were inserted in idealized positions and allowed to refine as riding on their parent C atoms, with C—H distances of 0.93 and 0.97 Å for aromatic and methylene H atoms, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SIR2004* (Burla *et al.*, 2005); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3072). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). *J. Appl. Cryst.* **37**, 335–338.
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.
Beddoes, R. L., Kettle, J. G. & Joule, J. A. (1994). *Acta Cryst.* C**50**, 1989–1992.
Boggs, J. E. & Kim, M. G. (1985). *J. Mol. Struct.* **119**, 271–279.
Braun, R. U., Zeitler, K. & Müller, T. J. J. (2001). *Org. Lett.* **3**, 3297–3300.
Bruker (1997). *SMART* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G. & Spagna, R. (2005). *J. Appl. Cryst.* **38**, 381–388.
Carabineiro, S. A., Bellabarba, R. M., Gomes, P. T. & Fonseca, I. M. (2006). *Catal. Lett.* **111**, 221–225.
Charette, A. B., Mathieu, S. & Martel, J. (2005). *Org. Lett.* **7**, 5401–5404.
Craig, L. C., Bulbrook, H. & Hixon, R. M. (1931). *J. Am. Chem. Soc.* **53**, 1831–1835.
Edwards, G. B., Yamanouchi, K., Kuchitsu, K., Sugie, M., Takeo, H., Matsumura, C., Ogawa, K. & Takeuchi, Y. (1985). *J. Mol. Spectrosc.* **111**, 301–319.
Esseveldt, B. C. J. van, van Delft, F. L., de Gelder, R. & Rutjes, F. P. J. T. (2003). *Org. Lett.* **5**, 1717–1720.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Fuganti, C., Gatti, F. G. & Serra, S. (2007). *Tetrahedron*, **63**, 4762–4767.
Fuhrer, W., Rasetti, V. & Rihs, G. (1985). *Helv. Chim. Acta*, **68**, 1235–1242.
Harrison, T. J. & Dake, G. R. (2005). *J. Org. Chem.* **70**, 10872–10874.
Hewton, C. E., Kimber, M. C. & Taylor, D. K. (2002). *Tetrahedron Lett.* **43**, 3199–3201.
Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.
Moriarty, R. M., Mitan, C. I., Branza-Nichita, N., Phares, K. R. & Parrish, D. (2006). *Org. Lett.* **8**, 3465–3467.
Rao, H. S. P. & Jothilingam, S. (2001). *Tetrahedron Lett.* **42**, 6595–6597.
Sessler, J. L., An, D., Cho, W.-S., Lynch, V. & Marquez, M. (2005). *Chem. Eur. J.* **11**, 2001–2011.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Steel, P. J., Katritzky, A. R., Greenhill, J. V., Hitchings, G. J. & Zhao, X. (1992). *Acta Cryst.* C**48**, 325–328.
Usubillaga, A., Zabel, V. & Watson, W. H. (1982). *Acta Cryst.* B**38**, 966–969.
Verniest, G., Claessens, S. & De Kimpe, N. (2005). *Tetrahedron*, **61**, 4631–4637.