

Intermolecular C—H··· π interactions in 1,5-diphenyl-3-(2-pyridyl)-2-pyrazoline

Miquel Barceló-Oliver,^{a*} Angel Terrón,^a Angel García-Raso,^a Nina Lah^b and Iztok Turel^b

^aDepartment of Chemistry and IUNICS, Universitat de les Illes Balears, Campus UIB, Cta. Valldemossa km 7.5, Edificada Mateu Orfila i Rotger, E-07122 Palma de Mallorca, Spain, and ^bFaculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia

Correspondence e-mail: miquel.barcelo@uib.es

Received 11 March 2010

Accepted 18 May 2010

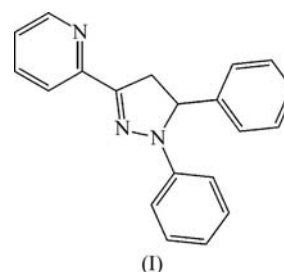
Online 26 May 2010

The title compound, C₂₀H₁₇N₃, is a derivative of 1,3,5-triaryl-2-pyrazoline and can act as an *N,N'*-bidentate ligand. This molecule features strong fluorescence that can be explained by an extended pyridyl—C=N—N—phenyl system. The three-dimensional structure is formed by means of an extended network of weak C—H··· π hydrogen bonds supported by π – π interactions.

Comment

1,3,5-Triaryl-2-pyrazolines present a wide range of interesting properties. They are used as whitening or brightening reagents (Wang *et al.*, 2001; Dørlars *et al.*, 1975) and as photosensitizers (Fushizaki & Sakikawa, 1971). Moreover, due to their fluorescence properties, these compounds have been utilized as fluorescence probes in some elaborate chemosensors (Bissell *et al.*, 1993; de Silva *et al.*, 1997). On the other hand, the fluorescent 3-(2-pyridyl)- analogues of triarylpyrazolines themselves can serve as *N,N'*-bidentate ligands for metal ions. Wang *et al.* (2001) reported that pyridylpyrazoline derivatives show specific fluorescent behaviour towards the Zn²⁺ ion among divalent transition metal ions, in particular, the 5-(4-cyanophenyl)- derivative. The stability constant in acetonitrile for the ZnL₂ complex was determined as 3.4 × 10¹¹ with a clear selectivity for other divalent ions such as copper(II) (Wang *et al.*, 2001). In a search of the Cambridge Structural Database (CSD, Version 5.31, February 2010 update; Allen, 2002), only two related structures were found with coordinates available: 1-(2-hydroxyethyl)-5-hydroxy-3-pyridin-2-yl-5-trifluoromethyl-4,5-dihydropyrazole (CSD refcode NIHDEO; Montoya *et al.*, 2007) and 2,3-[6-phenyl-1,4-bis(2-pyridyl)-2,3,5-triazahepta-1,4-diene-1,3-diyl]C₆₀fullerene carbon disulfide solvate (refcode NEPHAR; Miller *et al.*, 2001). Against this background, a crystallographic study of the title ligand, (I), is presented.

Compound (I) shows an extended pyridyl—C=N—N1—phenyl system, with atoms N2 and N32 present in an *anti* conformation (Fig. 1), as seen in 2,2'-bipyridyl. This conformation is probably forced by the repulsion between the two nonbonding electron pairs present on each N atom and by an intramolecular hydrogen-bond interaction between an N atom of the pyrazole ring and one H atom of the pyridine moiety, *viz.* C36—H36···N2. Atom N2 is the acceptor of another intramolecular nonstandard hydrogen bond (Steiner, 1996), *viz.* C12—H12···N2. For details of the intramolecular hydrogen-bond interactions in (I), see Table 1.



In order to achieve bidentate coordination to metal ions, an initial step from an *s-trans* to an *s-cis* conformation relative to the pyridyl imine group should be achieved, similar to that in 2,2'-bipyridyl. The C3—C31 distance [1.4620 (18) Å] is slightly shorter than a C—C single-bond length but longer than a typical C=C double-bond length (Allen *et al.*, 1995). In 2,2'-bipyridyl structures deposited in the CSD, this distance is 1.488 Å in BIPYRL04 (Kuhn *et al.*, 2002) and 1.504 Å in BIPYRL (Merritt & Schroeder, 1956). A comparison with the two 3-pyridyl-2-pyrazolines found in the CSD [1.471 Å in NEPHAR (*trans*; Miller *et al.*, 2001) and 1.455 Å in NIHDEO (*trans*; Montoya *et al.*, 2007)] suggests that although all the values for pyrazolines are shorter than those for 2,2'-bipyridyl, a rotation along the C3—C31 bond is possible.

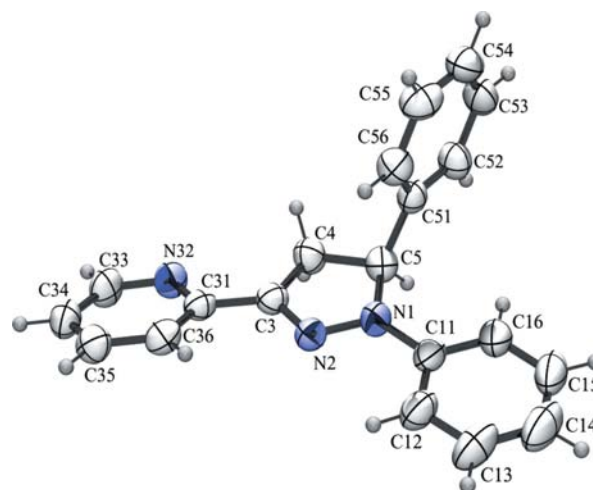
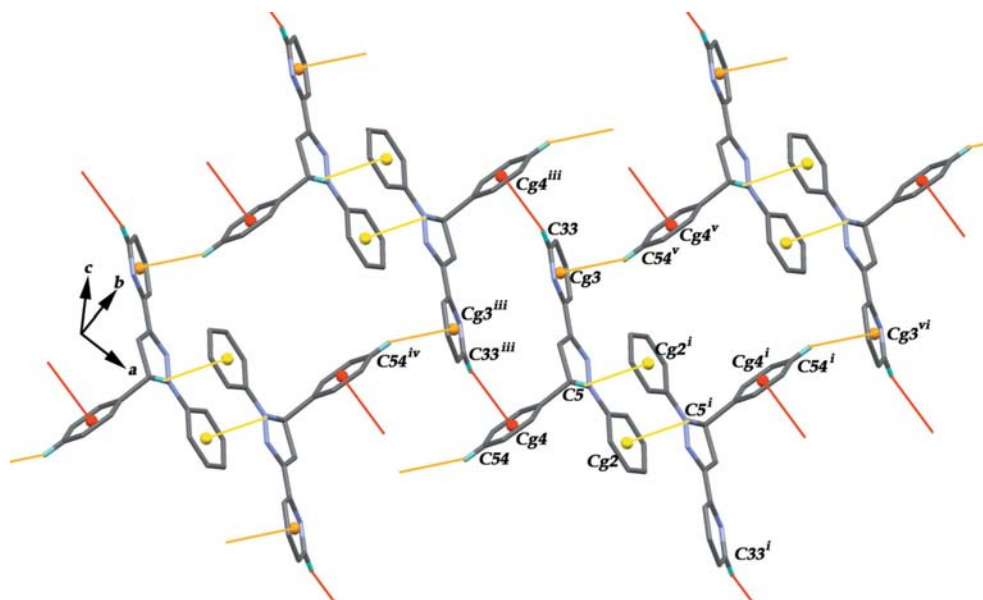


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

**Figure 2**

The C—H... π interactions in (I), forming a two-dimensional layer in the ab plane. Two C5—H5... $Cg2^i$ interactions, depicted in light shading (yellow in the electronic version of the paper), form centrosymmetric dimers, and two of these dimers interact by means of two C33—H33... $Cg4^{iii}$ interactions, depicted in dark shading (red), intertwined by C54—H54... $Cg3^{ii}$ interactions, depicted in mid-shading (orange). [Symmetry codes: (i) $1 - x, -y, 1 - z$; (ii) $x, -1 + y, z$; (iii) $-x, -y, 1 - z$; (iv) $-x, -1 - y, 1 - z$; (v) $x, 1 + y, z$; (vi) $1 - x, 1 - y, 1 - z$.]

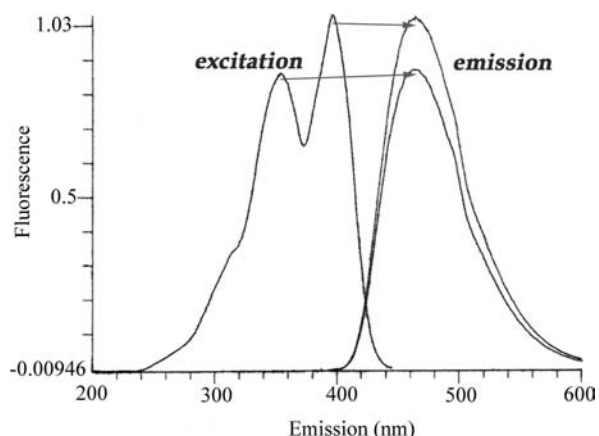
Although the five-membered pyrazoline ring cannot be planar, due to the presence of two Csp^3 atoms, and additionally in (I) it is twisted on the C4—C5 bond, a comparison of the deviations from the mean plane can be made. A correlation was found for the three structures: the longer the C3—C31 bond, the closer the atoms of the pyrazoline ring are to the calculated mean plane: in (I) from 0.008 to 0.051 Å, for NEPHAR from 0.002 to 0.008 Å and for NIHDEO from 0.054 to 0.161 Å.

Atom C56 is involved in an intramolecular interaction with the π system of the pyrazoline ring. This interaction can be described as a $C_{ar}-H \cdots \pi$ interaction (Desiraju & Steiner, 1999; Nishio *et al.*, 1998; Janiak, 2000), with the C—H group pointing rather to the middle of the N1—N2 bond (Table 2).

There are also intermolecular $C_{ar}-H \cdots \pi$ interactions in (I) (Table 2 and Fig. 2). Atom C54 of the phenyl ring attached to atom C5 interacts with the pyridyl ring of an adjacent molecule, and atom C33 of the pyridyl ring interacts with the phenyl ring attached to atom C5 of a neighbouring molecule. To complete the two-dimensional network, another C—H... π interaction is found in the structure of (I); a centrosymmetric dimer is formed by means of two interactions involving the pyrazoline rings, with the C5 atoms as donors, and N1-bonded phenyl rings, corresponding to two different molecules (see Fig. 2). The centrosymmetric dimer is also reinforced by stacking interactions between the π system of the pyrazoline ring and the phenyl ring bonded to N1 (Table 3). By means of these interactions, two-dimensional layers are present, staggered in the c direction. The contact distances and geometric characteristics of these interactions seem to be a good example of C—H... π interactions in organic compounds.

The molecule of (I) is strongly fluorescent, probably due to the extended pyridyl—C3=N2—N1—phenyl system already mentioned. In chloroform, this compound presents both excitation and emission bands in the visible part of the spectrum ($\lambda_{exc} = 397$ nm and $\lambda_{em} = 464$ nm) (Fig. 3). Moreover, these fluorescent properties are pH sensitive, disappearing under acidic conditions but not in the presence of a base.

In conclusion, the structure of (I) described here, its theoretically good capacity for binding to metal ions (Wang *et al.*, 2001) and its fluorescent properties support the idea that 1,5-diphenyl-3-(2-pyridyl)-2-pyrazoline could in future be an interesting means of studying Zn^{II} or other metal ions by means of fluorescent techniques.

**Figure 3**

The fluorescent properties of (I).

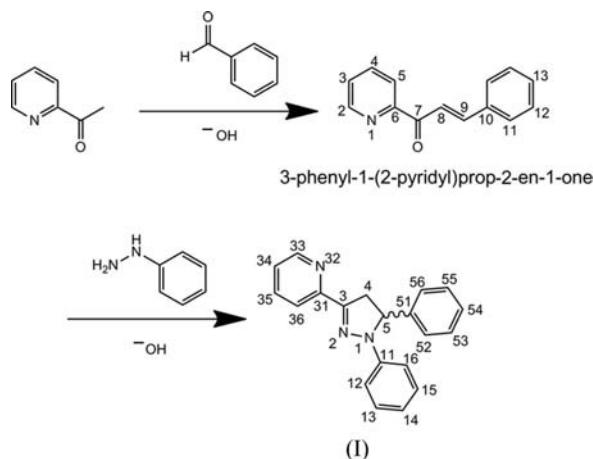


Figure 4

The synthetic pathway of (I), showing the numbering scheme used throughout this article.

Experimental

1,5-Diphenyl-3-(2-pyridyl)-2-pyrazoline, (I), was obtained in a two-step synthesis, as indicated in Fig. 4.

For the preparation of 3-phenyl-1-(2-pyridyl)prop-2-en-1-one, benzaldehyde (3.6 g, 34 mmol) and 2-acetylpyridine (2 g, 17 mmol) were added to a solution of KOH (0.8 g) in EtOH–H₂O (50:50 v/v, 10 ml). The mixture was sealed and stirred for 4 h. At first, the solution showed a bright-yellow colour and, finally, two different phases were present, one of them with an oily aspect. This phase turned solid when the mixture was frozen in an ice bath. A yellow powder was obtained, filtered off and then washed with cold EtOH–H₂O (50:50 v/v) (yield 63%). Analysis found: C 78.78, H 5.22, N 6.53%; calculated for C₁₄H₁₁NO·0.25H₂O: C 78.67, H 5.42, N 6.55%.

For the preparation of (I), 3-phenyl-1-(2-pyridyl)prop-2-en-1-one (0.56 g, 2.5 mmol) and phenylhydrazine (0.43 g, 4 mmol) were added to a solution of KOH (0.20 g) in EtOH (20 ml) and the mixture was refluxed for 24 h. The resulting brown solution was left for 1–2 d at room temperature and a brown product appeared which was filtered off. The filtrate was allowed to evaporate slowly and both a microcrystalline yellow product and yellow crystals of (I), suitable for X-ray diffraction studies, were formed [yield of (I) 33%]. Analysis found: C 79.90, H 5.70, N 13.84%; calculated for C₂₀H₁₇N₃: C 80.24, H 5.72, N 14.04%. Spectroscopic data for both 3-phenyl-1-(2-pyridyl)prop-2-en-1-one and (I) are available in the archived CIF.

Crystal data

C ₂₀ H ₁₇ N ₃	$V = 1612.46 (6) \text{ \AA}^3$
$M_r = 299.37$	$Z = 4$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 13.2312 (3) \text{ \AA}$	$\mu = 0.07 \text{ mm}^{-1}$
$b = 10.4394 (2) \text{ \AA}$	$T = 294 \text{ K}$
$c = 11.7282 (2) \text{ \AA}$	$0.25 \times 0.25 \times 0.25 \text{ mm}$
$\beta = 95.518 (2)^\circ$	

Data collection

Nonius KappaCCD area-detector diffractometer	6706 measured reflections
Absorption correction: multi-scan (DENZO and SCALEPACK; Otwinowski & Minor, 1997)	3678 independent reflections
$T_{\min} = 0.933$, $T_{\max} = 0.982$	2543 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.023$

Table 1
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C12–H12 \cdots N2	0.93	2.49	2.800 (2)	100
C36–H36 \cdots N2	0.93	2.67	2.911 (2)	96

Table 2
C–H $\cdots\pi$ interactions (\AA , $^\circ$).

Cg1, Cg2, Cg3 and Cg4 are the centroids of the N1/N2/C3–C5, C11–C16, C31/N32/C33–C36 and C51–C56 rings, respectively.

$D-H \cdots Cg$	$D-H$	$H \cdots Cg$	$D-H \cdots Cg$	$D-H \cdots Cg$
C56–H56 \cdots Cg1	0.93	2.67	2.9535 (17)	98
C5–H5 \cdots Cg2 ⁱ	0.98	2.83	3.6326 (16)	140
C54–H54 \cdots Cg3 ⁱⁱ	0.93	2.73	3.5548 (18)	149
C33–H33 \cdots Cg4 ⁱⁱⁱ	0.93	2.77	3.6018 (16)	149

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

Table 3
Main π – π interaction (\AA , $^\circ$).

Cg1 and Cg2 are the centroids of the N1/N2/C3–C5 and C11–C16 rings, respectively. As in PLATON (Spek, 2009), α is the dihedral angle between planes I and J , β is the angle between the $CgI \rightarrow CgJ$ vector and the normal to the plane I , γ is the angle between the $CgI \rightarrow CgJ$ vector and the normal to the plane J , CgI -Perp is the perpendicular distance of CgI from ring J , CgJ -Perp is the perpendicular distance of CgJ from ring I , and the slippage S is the distance between CgI and the perpendicular projection of CgJ on ring I .

$CgI \cdots CgJ$	$Cg \cdots Cg$	α	β	γ	CgI -Perp	CgJ -Perp	S
$Cg1 \cdots Cg2^i$	3.9840 (10)	3.47 (8)	27.49	27.48	3.5347 (6)	3.5341 (7)	

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

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.047$	208 parameters
$wR(F^2) = 0.133$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.12 \text{ e \AA}^{-3}$
3678 reflections	$\Delta\rho_{\text{min}} = -0.15 \text{ e \AA}^{-3}$

Monoclinic cell parameters were chosen according to the ‘best choice’ criterion for monoclinic structures (Parthé & Gelato, 1985). All H atoms were placed in geometrically calculated positions and refined using a riding model, with $C-H = 0.93\text{--}0.98 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: COLLECT (Nonius, 1998); cell refinement: DENZO and SCALEPACK (Otwinowski & Minor, 1997); data reduction: DENZO and SCALEPACK; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97 and PLATON (Spek, 2009).

The authors thank the Vicerectorat de Investigació i Política Científica of the University of the Balearic Islands (project No. UIB2005/5), the Conselleria d’Economia, Hisenda i Innovació (Competitive Groups grant) of the Government of the Balearic Islands, and the Direcció General de Investigació Científica y Técnica of the Spanish authorities and FEDER

funds (project No. CTQ2006-09339/BQU) for their generous financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3030). Services for accessing these data are described at the back of the journal.

References

- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1995). *International Tables for Crystallography*, Vol. C, edited by A. J. C. Wilson, pp. 685–706. Dordrecht: Kluwer Academic Publishers.
- Bissell, R. A., de Silva, A. P., Gunaratne, H. Q. N., Lynch, P. L. M., Maguire, G. E. M., McCoy, C. P. & Sandanayake, K. R. A. S. (1993). *Top. Curr. Chem.* **168**, 223–264.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*. New York: Oxford University Press Inc.
- Dorlars, H., Schellhammer, C. W. & Schroeder, J. (1975). *Angew. Chem. Int. Ed. Engl.* **14**, 665–679.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fushizaki, Y. & Sakikawa, K. (1971). Jpn Patent JP 46003577.
- Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.
- Kuhn, F. E., Groarke, M., Bencze, E., Herdtweck, E., Prazeres, A., Santos, A. M., Calhorda, M. J., Romao, C. C., Goncalves, I. S., Lopes, A. D. & Pillinger, M. (2002). *Chem. Eur. J.* **8**, 2370–2383.
- Merritt, L. L. & Schroeder, E. (1956). *Acta Cryst.* **9**, 801–804.
- Miller, G. P., Tetreau, M. C., Olmstead, M. M., Lord, P. A. & Balch, A. L. (2001). *Chem. Commun.* pp. 1758–1759.
- Montoya, V., Pons, J., García-Anton, J., Solans, X., Font-Bardia, M. & Ros, J. (2007). *J. Fluorine Chem.* **128**, 1007–1011.
- Nishio, M., Hirota, M. & Umezawa, Y. (1998). *The C–H... π Interaction (Evidence, Nature and Consequences)*. New York: Wiley–VCH.
- Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
- Parthé, E. & Gelato, L. M. (1985). *Acta Cryst.* **A41**, 142–151.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Silva, A. P. de, Gunaratne, H. Q. N., Gunnlaugsson, T., Huxley, A. J., McCoy, C. P., Rademacher, J. T. & Rice, T. E. (1997). *Chem. Rev.* **97**, 1515–1566.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Steiner, Th. (1996). *Crystallogr. Rev.* **6**, 1–57.
- Wang, P., Onozawa-Komatsuzaki, N., Himeda, Y., Sugihara, H., Arakawa, H. & Kasuga, K. (2001). *Tetrahedron Lett.* **42**, 9199–9201.