Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

A unique tautomer of 1-*n*-hexyl-3-phenyl-1*H*-pyrazol-5-ol

Julio Belmar,[a]* Claudio Jiménez,[a] C. Ruiz-Pérez,[b] F. S. Delgado[b] and Ricardo Baggio[c]

[a]Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad de Concepción, Casilla 160-C, Concepción, Chile, [b]Laboratorio de Rayos X y Materiales Moleculares, Departamento de Física Fundamental II, Facultad de Física, Universidad de La Laguna, Tenerife, Spain, and [c]Departamento de Física, Comisión Nacional de Energía Atómica, Buenos Aires, Argentina
Correspondence e-mail: jbelmar@udec.cl

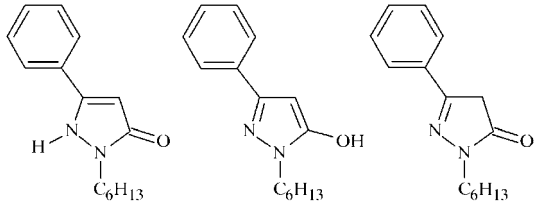
Received 10 August 2006
Accepted 17 August 2006
Online 12 September 2006

In the title compound, $C_{15}H_{20}N_2O$, the bond distances and angles are consistent with the presence of the hydroxy tautomer. This tautomer was unambiguously determined by the clear presence of a H atom bonded to oxygen, as well as the total absence of any residual electron density around the N atom in the heterocycle, thus precluding any possibility of desmotropism.

Comment

Pyrazolones are an important family of organic heterocyclic compounds (Elguero, 1996), which have attracted much attention due to their applications as drugs (Gürzov *et al.*, 2000), extractants (Marchetti *et al.*, 2005; Pettinari *et al.*, 2000) or dyes (Emeleus *et al.*, 2001), and because of the prototropic tautomerism they exhibit (Elguero *et al.*, 1976). As a consequence, they have been extensively studied, both in solution and in the crystalline phase (Chmutova *et al.*, 2001). Unsubstituted pyrazolones and 1-arylpyrazolones (and their derivatives) are commonly described in the literature, while their 1-alkyl homologues are seldom mentioned. This situation is quite unfortunate, since 1-alkylpyrazolones are more soluble than their 1-aryl counterparts, which would make them valuable products. It is worthy of note that 3-phenylpyrazolones are very scarce in the literature, with only very few reported examples (Belmar *et al.*, 1999; Marchetti *et al.*, 2005). Therefore, 1-*n*-alkyl-3-phenyl-5-pyrazolones are even rarer compounds.

Some years ago, a project aimed at the synthesis of 1-alkyl-3-methyl-5-pyrazolones and their derivatives was initiated (Bartulin *et al.*, 1992). A few years later, 1-*n*-butyl- and 1-*n*-hexyl-3-phenyl-5-pyrazolone were synthesized (Belmar *et al.*, 1999). The new objective was to observe the effect, if any, on the tautomeric equilibrium of changing from a methyl group to a phenyl group at position 3. However, the structures of these new compounds could not be fully established in dimethyl sulfoxide solution, and it was not possible to decide between the NH and OH tautomers, or indeed whether the two forms were both present as an equilibrium mixture. In chloroform solution, however, the presence of the CH form was clearly established (see scheme). These results are consistent with previous observations on 1-*n*-alkyl-3-methyl-5-pyrazolones, whose solid-state structures could not be firmly established using IR spectroscopy.



It has already been reported (Foces-Foces *et al.*, 1997) that, in the crystalline state, 1-phenyl-3-methyl-5-pyrazolone exhibits desmotropy, *i.e.* the NH and OH tautomers co-exist in the unit cell. On the other hand, the 1-(4-bromophenyl) analogue occurs only in the NH form in the solid state. Thus, it is interesting to establish the solid-state structures of similar related compounds. As a new contribution to the knowledge of tautomerism in pyrazolone derivatives, we report here the first crystal structure of a 1-alkyl-3-phenyl-5-hydroxypyrazole, namely that of 1-*n*-hexyl-3-phenyl-1*H*-pyrazol-5-ol, (I) (Fig. 1).

The clear presence of the hydroxyl H atom in the difference Fourier synthesis and the absence of any residual electronic density in the vicinity of N2 confirm that compound (I)

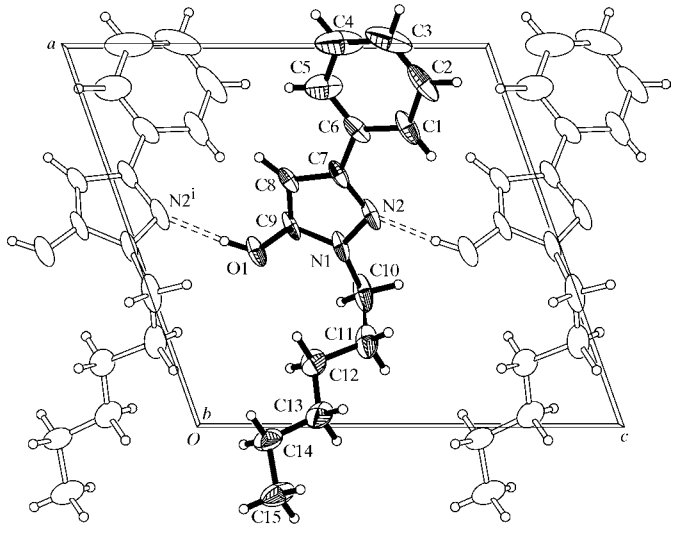


Figure 1
A plot of the structure of (I), viewed down *b*, showing the way in which the chains (running along *c*) are formed. Displacement ellipsoids are drawn at the 40% probability level. Only the reference molecule in the asymmetric unit has been drawn with full ellipsoids, symmetry-related molecules being represented with open ellipsoids. The strong intermolecular O—H···N bond is represented by a double dashed line. [Symmetry code: (i) $x, -y+1, z-\frac{1}{2}$.]

 DOI: 10.1107/S0108270106032926

crystallizes as a pure hydroxyl tautomer and that no desmotropism is present (Foces-Foces *et al.*, 1997). Moreover, the bond distances around the heterocycle (Table 1) are fully consistent with this conclusion: N2—C7 and C8—C9 correspond to well defined double bonds, while C7—C8, even though it is shorter than in any of the closely related compounds (Belmar *et al.*, 2004; Bothe *et al.*, 2001), exhibits significant single-bond character. Finally, C9—O1 is clearly a single bond, as expected from the presence of H1 bonded to O1. Fig. 2 shows the V-shaped nature of the molecule, with alkylic atom C10 at the vertex of the V. The aromatic part is almost planar, with a maximum deviation of 0.08 (1) Å (for atom N1) from the mean plane containing both groups. Also effectively planar is the fully extended alkyl chain, where the maximum deviation from planarity is 0.09 (1) Å for atom C10. The dihedral angle between the aryl and alkyl planes is 65.9 (1)°.

The simultaneous presence in the heterocycle of a hydroxyl group, a quite efficient hydrogen-bond donor, and a non-protonated N atom, a good acceptor for this type of interaction, results in the formation of a very strong O—H···N bond linking the molecules related by the *c*-glide into tightly connected chains running along [001]. The interaction is strong enough to 'freeze' the H atom, permitting its easy location in difference maps and also allowing its free refinement without any restraints. The V-shaped molecules lie on both sides of the glide plane, with their vertices almost aligned on the plane and in a (displaced) mirror-like fashion. Thus, when observed in projection down [001], an 'X-like' view of the array is obtained (Fig. 2). This particular shape of the chains allows them to interdigitate neatly along [100], with alkyl groups in one chain fitting the voids left by adjacent aromatic groups in neighbouring chains. This interdigitation in consecutive chains along [100] defines a pseudo-two-dimensional structure parallel to (010), centred on $y = 0$ and $\frac{1}{2}$ (Fig. 2). The planes are well separated along [010] and lateral contacts between these structures are purely of the van der Waals type.

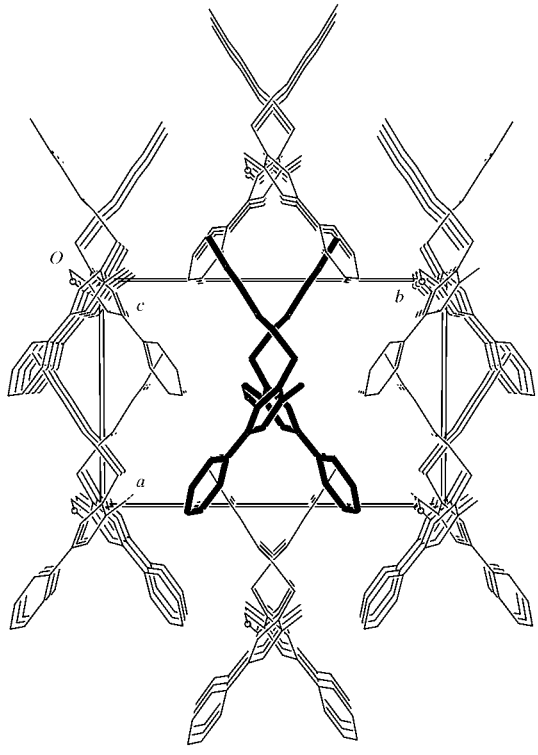


Figure 2
A packing diagram, viewed down *c*, showing the stacking of the X-shaped chains. For clarity, one single chain is shown with heavy lines. Note the way in which vertically displaced chains interdigitate to form broad well separated two-dimensional structures.

Experimental

1-*n*-Hexyl-3-phenylpyrazol-5-ol was obtained in a two-step process, as reported elsewhere (Belmar *et al.*, 1999). The product was crystallized from an ethanolic solution saturated with water at boiling temperature [yields 80% (first step, 3-phenyl-5-pyrazolone) and 40% (second step), m.p. 434–437 K]. Single crystals were selected from the crystallized material.

Crystal data

$C_{15}H_{20}N_2O$
$M_r = 244.33$
Monoclinic, *Cc*
$a = 10.0979$ (4) Å
$b = 13.4026$ (7) Å
$c = 10.6047$ (4) Å
$\beta = 109.479$ (3)°
$V = 1353.07$ (10) Å^3
$Z = 4$
$D_x = 1.199$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.08$ mm^{-1}
$T = 170$ (2) K
Block, colourless
0.28 × 0.22 × 0.17 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
3616 measured reflections
1167 independent reflections
906 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.109$
$S = 1.13$
1167 reflections
169 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 1.0265P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.17$ e Å^{-3}
$\Delta\rho_{min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.016 (2)

Table 1
Selected bond lengths (Å).

O1—C9	1.336 (5)	C2—C3	1.377 (9)
N1—C9	1.355 (5)	C3—C4	1.351 (9)
N1—N2	1.385 (4)	C4—C5	1.367 (8)
N1—C10	1.448 (6)	C5—C6	1.371 (7)
N2—C7	1.336 (6)	C6—C7	1.470 (5)
C1—C2	1.392 (7)	C7—C8	1.407 (5)
C1—C6	1.392 (6)	C8—C9	1.359 (6)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···N2^{i}	0.86 (5)	1.80 (5)	2.658 (5)	176 (5)

Symmetry code: (i) $x, -y+1, z-\frac{1}{2}$.

Those H atoms defined by the stereochemistry were placed in their theoretical positions (Csp^2—H = 0.97 Å and Csp^3—H = 0.96 Å) and allowed to ride. The methyl group was allowed to rotate around its local threefold axis. Atom H1 attached to O1 was found in a difference Fourier map and refined freely. Isotropic displacement parameters for all H atoms except H1 were defined as U_{iso}(H) = xU_{eq}(parent), with x = 1.2 or 1.5 for non-methyl and methyl H atoms, respectively. As no significant anomalous scattering effects were present, Friedel opposites were merged before refinement. This resulted in a less than ideal data-to-parameter ratio (an approximate value of 7).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*/*PC* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

This research was supported by the Universidad de Concepción through a grant from Dirección de Investigación (PDI 205.023.042-1.0) and Ministerio Español de Educación y Ciencia (MAT2004-03112). The authors are greatly indebted to the Spanish Research Council (CSIC) for provision of a free-of-charge license for the Cambridge Structural Database (Allen, 2002) and *ConQuest* and *IsoStar* software.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3042). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bartulin, J., Belmar, J. & León, G. (1992). *Bol. Soc. Chil. Quim.* **37**, 13–18.
Belmar, J., Alderete, J., Parra, M. & Zúñiga, C. (1999). *Bol. Soc. Chil. Quim.* **44**, 367–374.
Belmar, J., Pérez, F. R., Moreno, Y. & Baggio, R. (2004). *Acta Cryst.* C**60**, o705–o708.
Bothe, U., Rudbeck, H. C., Tanner, D. & Johannsen, M. (2001). *J. Chem. Soc. Perkin Trans. 1*, p. 3305.
Bruker (2001). *SAINT* (Version 6.02a) and *SMART* (Version 5.624). Bruker AXS Inc., Madison, Wisconsin, USA.
Chmutova, G. A., Kaetaeva, O. N., Ahlbrecht, H., Kurbangalieva, A. R., Movchan, A. I., Lenstra, A. T. H., Geise, H. J. & Livinov, I. A. (2001). *J. Mol. Struct.* **570**, 215–223.
Elguero, J. (1996). *Comprehensive Heterocyclic Chemistry II: Pyrazoles*, Vol. 3, edited by A. R. Katrizky, C. W. Rees & E. F. V. Scriven, pp. 1–75. Oxford: Pergamon Press.
Elguero, J., Marzin, C., Katritzky, A. R. & Linda, P. (1976). *Advances in Heterocyclic Chemistry: The Tautomerism of Heterocycles*, Suppl. 1, pp. 313–336. New York: Academic Press.
Emeleus, L. C., Cupertino, D. C., Harris, S. G., Owens, S., Parsons, S., Stewart, R. M. & Tasker, P. A. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1239–1245.
Foces-Foces, C., Fontenas, C., Elguero, J. & Sobrados, I. (1997). *An. Quim. Int. Ed.* **93**, 219–224.
Gürzov, A., Demirayak, S., Capaan, G., Erol, K. & Vural, K. (2000). *Eur. J. Med. Chem.* **35**, 359–364.
Marchetti, F., Pettinari, R. & Pettinari, C. (2005). *Coord. Chem. Rev.* **249**, 2909–2945.
Pettinari, C., Marchetti, F., Cingolari, A., Leonesi, D., Troyanov, S. & Drozov, A. (2000). *J. Chem. Soc. Dalton Trans.* pp. 831–836.
Sheldrick, G. M. (1994). *SHELXTL*/*PC*. Version 5.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.