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A new polymorph of 3-phenylpyrazole

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.092
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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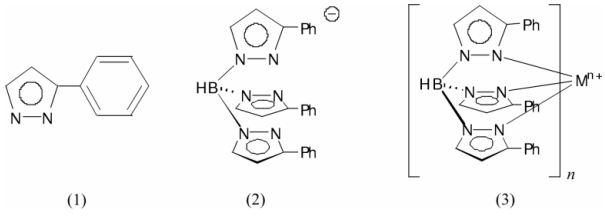
A new polymorph of 3-phenylpyrazole, $C_9H_8N_2$, is described. Whereas the already known polymorph has $Z' = 6$, the new one has $Z' = 4$. The pyrazole rings of the four molecules in the asymmetric unit are connected by N—H···N hydrogen bonds to form cyclic four-membered clusters. In two pyrazole rings, it is the N atom in position 1 that carries the H atom, whereas in the other two the N atom in position 2 carries the H atom. There are no further short contacts between symmetry-equivalent clusters.

Comment

Recently, we have reported the X-ray crystal structure analysis of 3-phenylpyrazole, $C_9H_8N_2$, (1) (Haghiri *et al.*, 2002). Here we describe the X-ray crystal structure analysis of a new polymorph of 3-phenylpyrazole, (1). Tris(1-pyrazolyl)borates ('scorpinates') were invented by Trofimenko more than 30 years ago, and are today well established as ligands in coordination chemistry (Trofimenko, 1993). Scorpinates now find applications in a wide range of chemistry, from modeling the active site of metal–enzymes, through analytical chemistry and organic synthesis to catalysis and materials science (Edelmann, 2001).



(1) (2) (3)

Given this background, we are interested in the synthesis of transition metal complexes (3) with hydrotris(3-phenylpyrazol-1-yl)borate, (2), as the ligand (see Scheme). We have therefore prepared 3-phenylpyrazole as a starting material several times. A new polymorph of 3-phenylpyrazole was obtained after recrystallization from CH_3OH instead of from CH_2Cl_2.

The asymmetric unit of (1) contains four independent molecules, labeled *A* to *D*. It is interesting to note that in molecules *A* and *B* the N atom in position 1 carries an H atom, whereas in molecules *C* and *D* the N atom in position 2 carries the H atom. The pyrazole and phenyl groups of each molecule are approximately planar. The angles between the planes of the pyrazole and phenyl rings are 10.7 (1), 17.4 (1), 16.9 (1) and 14.95 (6)° for molecules *A* to *D*, respectively. The crystal structure is built up of cyclic clusters of these four molecules,

held together by N—H···N hydrogen bonds (Fig. 1 and Table 1).

Experimental

The title compound was synthesized according to literature procedures (Buchner & Hachumian, 1902). X-ray quality crystals were obtained after recrystallization from CH_3OH at ambient temperature.

Crystal data

$C_9H_8N_2$
M_r = 144.17
Triclinic, $P\overline{1}$
a = 9.5745 (13) Å
b = 10.3359 (12) Å
c = 17.132 (2) Å
α = 85.693 (10)°
β = 75.609 (10)°
γ = 72.102 (10)°
V = 1562.7 (3) Å^3
Z = 8
D_x = 1.226 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7377 reflections
θ = 3.5–25.2°
μ = 0.08 mm^{-1}
T = 173 (2) K
Block, colorless
0.31 × 0.15 × 0.11 mm

Data collection

Stoe IPDS II two-circle diffractometer
ω scans
Absorption correction: none
12794 measured reflections
5573 independent reflections
3329 reflections with $I > 2\sigma(I)$
R_{int} = 0.059
θ_{max} = 25.2°
$h = -11 \rightarrow 11$
$k = -11 \rightarrow 12$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.092
S = 0.88
5573 reflections
398 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0337P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0084 (9)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1A—H1A···N2B	0.88	2.04	2.909 (2)	168
N1B—H1B···N1C	0.88	2.00	2.863 (2)	165
N2C—H2C···N1D	0.88	2.06	2.894 (3)	158
N2D—H2D···N2A	0.88	2.00	2.840 (2)	160

All H atoms were located in a difference Fourier synthesis and were refined with fixed individual displacement parameters [U_{iso}(H) = 1.2U_{eq}(N,C)], using a riding model with N—H = 0.88 Å and C—H = 0.95 Å.

Data collection: *X-AREA* (Stoe & Cie, 2001); cell refinement: *X-AREA*; data reduction: *X-AREA*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97.

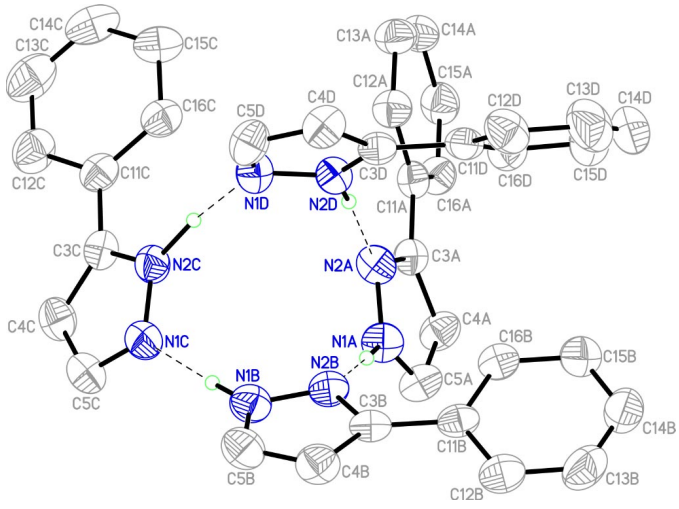


Figure 1
Perspective view of the four-membered cluster of the title compound, with the atom-numbering scheme; displacement ellipsoids are drawn at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity.

References

Buchner, E. & Hachumian, C. (1902). *Chem. Ber.* **35**, 36–42.
Edelmann, F. T. (2001). *Angew. Chem. Int. Ed. Engl.* **40**, 1656–1659.
Haghiri, A., Lerner, H.-W., Wagner, M. & Bats, J. W. (2002). *Acta Cryst.* E**58**, o1378–o1380.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Stoe & Cie (2001). *X-AREA*. Stoe & Cie, Darmstadt, Germany.
Trofimenko, S. (1993). *Chem. Rev.* **93**, 943–980.