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2-[Bis(pyrazol-1-yl)methyl]-4-*tert*-butyl-6-(phenylsulfanyl)phenol

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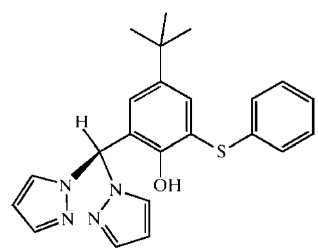
The title compound, $C_{23}H_{24}N_4OS$, contains a highly asymmetric bifurcated intramolecular hydrogen bond between the hydroxy group and two pyrazole N atoms. The compound associates into centrosymmetric dimers in the crystal through two unique C—H$\cdots\pi$ interactions, which are in turn linked into a (6,3)-network through an additional intermolecular C—H$\cdots$N hydrogen bond.

Comment

Heteroleptic tripodal di- and tripyrazol-1-yl derivatives (so-called 'heteroscorpionates') are finding increasing use as ligands to transition metals (Trofimenko, 1999; Otero, Fernández-Baeza, Antiñolo, Tejeda & Lara-Sánchez, 2004). Bis(pyrazolyl)methane ligands bearing alkoxy, phenoxy and carboxylate functions have been of particular interest as models for mixed-donor metal biosites (see, for example, Beck *et al.*, 2003; Hammes *et al.*, 2003, 2004; Hoffman *et al.*, 2004) and as protecting groups in organometallic compounds (see, for example, Caballero *et al.*, 2004; Otero *et al.*, 2003; Otero, Fernández-Baeza, Antiñolo, Tejeda, Lara-Sánchez *et al.*, 2004). We have prepared the title compound, (I), as part of our continuing investigation of chemistry related to the copper enzyme galactose oxidase (Halcrow *et al.*, 1999; Liu *et al.*, 2002; Sylvestre *et al.*, 2005), which contains a biologically unique



(I)

ortho-(alkylsulfanyl)tyrosyl free radical in its active site (Whittaker, 2003). Three other 2-[bis(pyrazol-1-yl)methyl]-phenol derivatives have also been crystallographically characterized by Carrano's group (Higgs & Carrano, 1997, 2002; Shirin & Carrano, 2004).

Compound (I) (Fig. 1) was prepared from 5-*tert*-butyl-2-hydroxy-3-(phenylsulfanyl)benzaldehyde (Wang & Stack, 1996) and di(pyrazol-1-yl) ketone (Byers *et al.*, 1990) by Carrano's procedure (Higgs & Carrano, 1997), and crystallized from a 1:1 diethyl ether/pentane mixture. All bond lengths and angles within the molecule lie within their usual ranges. There is a bifurcated intramolecular hydrogen bond between hydroxy group O1 and pyrazole atoms N27 and N28, although the latter interaction clearly dominates. Interestingly, this type of hydrogen bond is only observed in one of the other three known 2-[bis(pyrazol-1-yl)methyl]phenol crystal structures (Higgs & Carrano, 2002), despite the apparent proximity of these groups in this class of molecule. As is usual in diaryl sulfides, the two aryl groups C1–C6 and C1*P*–C6*P* are close to being perpendicular, the dihedral angle between their planes being 78.57 (6)°. This configuration does not give rise to a significant intramolecular edge-to-face interaction between these two rings, however, since atom H5 lies 3.00 Å from the centroid of the C1*P*–C6*P* ring. This is slightly longer than the sum of the van der Waals radii for a H atom (1.2 Å) and an aromatic ring (1.7 Å; Pauling, 1960).

Neighbouring molecules related by ($-x$, $1 - y$, $-z$) associate into centrosymmetric dimers through two weak intermolecular interactions involving phenyl group C1*P*–C6*P* (Fig. 2). The first is an intermolecular hydrogen bond, *viz.* C5*P*—H5*P*$\cdots$N27^{i} [symmetry code: (i) $-x, 1 - y, -z$; Table 1]. This contact is probably best considered as a C—H$\cdots\pi$ interaction, since the donor phenyl group C5*P*—H5*P* and acceptor pyrazole group N27^{i}—C31^{i} are nearly perpendicular, with a dihedral angle of 80.57 (7)°. The second is another C—H$\cdots\pi$ interaction between atom H6*P* and the C1^{i}–C6^{i} ring, with a H6*P*$\cdots$C4^{i} distance of 2.87 Å and a C6*P*—H6*P*$\cdots$C4^{i} angle of 159° [as before, the dihedral angle between the planes

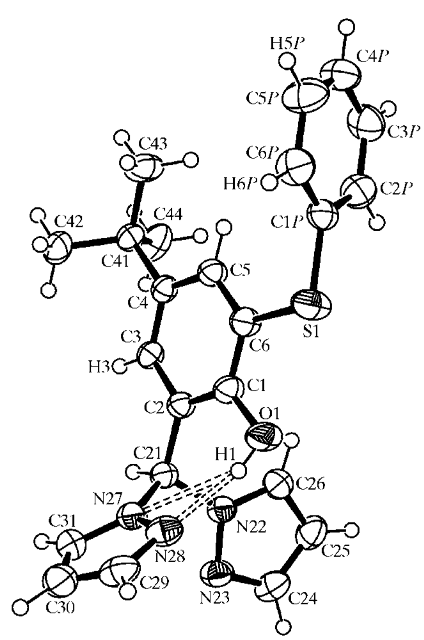


Figure 1
A view of the asymmetric unit in the crystal structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme employed. H atoms have arbitrary radii and specific H atoms referred to in the *Comment* are labelled.

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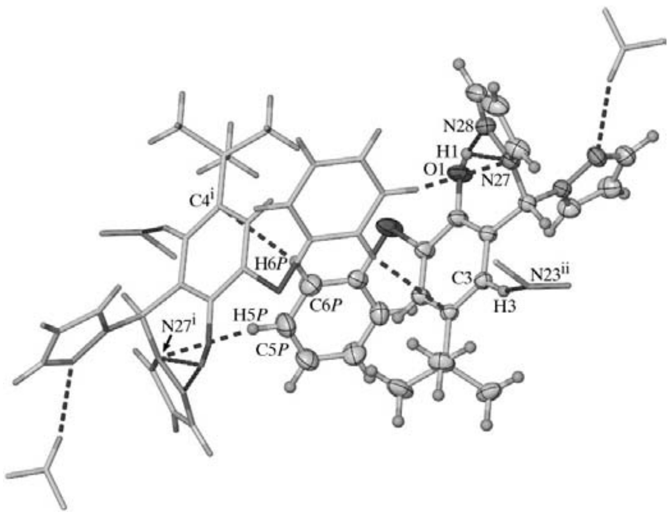

Figure 2
The weak association of molecules of (I) into centrosymmetric dimers through C—H$\cdots\pi$ interactions. One of the two molecules has been de-emphasized for clarity. The view is approximately perpendicular to the (011) crystallographic plane, with the *a* axis horizontal. [Symmetry code: (i) $-x, 1-y, -z$.]

of the aryl groups C1*P*–C6*P* and C1^{i}–C6^{i} is 78.57 (6)°]. The H5*P*$\cdots$N27^{i} and H6*P*$\cdots$C4^{i} distances are both 0.1–0.2 Å shorter than the sum of the van der Waals radii of a H atom (1.2 Å) and an aromatic ring (1.7 Å; Pauling, 1960). Adjacent dimers in the crystal structure associate into sheets through a C—H$\cdots$N hydrogen bond, *viz*. C3—H3$\cdots$N23^{ii} [symmetry code: (ii) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$]. In contrast to the C5*P*—H5*P*$\cdots$N27^{i} interaction, atom H3 is clearly positioned to interact with the lone pair of the pyridine-type atom N23^{ii}. The overall effect of these interactions is to link adjacent molecules in the crystal structure into puckered (6,3) herring-bone sheets running parallel to the (102) crystal plane.

Experimental

A mixture of 5-*tert*-butyl-2-hydroxy-3-(phenylsulfanyl)benzaldehyde (1.5 g, 5.2 mmol), di(pyrazol-1-yl) ketone (1.3 g, 5.2 mmol) and $CoCl_2 \cdot 6H_2O$ (12 mg, 0.05 mmol) was heated under N_2 to 373 K until evolution of CO_2 ceased. The resulting pink solid was cooled, dissolved in CH_2Cl_2, and washed with water and brine. The organic layers were dried over Na_2SO_4 and evaporated to dryness to leave a yellow oil. Crystallization of the crude product from a 1:1 diethyl ether/pentane solvent mixture afforded yellow crystals (yield 0.74 g, 35%). Analysis found: C 68.3, H 6.0, N 13.8%; calculated for $C_{23}H_{24}N_4OS$: C 68.2, H 6.2, N 14.0%. ^{1}H NMR ($CDCl_3$, 298 K): δ 1.18 [*s*, 9H, $C(CH_3)_3$], 6.31 (pseudo-*t*, 2.4 Hz, 2H, Pz H4), 7.01 (*d*, 2.1 Hz, 1H, Ph H3), 7.14–7.27 (*m*, 5H, C_6H_5), 7.46 (*d*, 2.1 Hz, 1H, Ph H5), 7.58 and 7.61 (both *d*, 2.4 Hz, 2H, Pz H3 and Pz H5), 7.71 (*s*, 1H, CH).

Crystal data

$C_{23}H_{24}N_4OS$
$M_r = 404.52$
Monoclinic, $P2_1/c$
$a = 13.6486$ (2) Å
$b = 9.3529$ (1) Å
$c = 17.8913$ (3) Å
$\beta = 109.214$ (1)°
$V = 2156.67$ (5) Å^3
$Z = 4$
$D_x = 1.246$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 43 089 reflections
$\theta = 2.4$–27.5°
$\mu = 0.17$ mm^{-1}
$T = 150$ (2) K
Rectangular prism, yellow
0.66 × 0.53 × 0.43 mm

Data collection

Nonius KappaCCD area-detector diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.594$, $T_{max} = 0.929$
43 089 measured reflections
4921 independent reflections
4101 reflections with $I > 2\sigma(I)$
$R_{int} = 0.072$
$\theta_{max} = 27.5°$
$h = -17 \rightarrow 17$
$k = -12 \rightarrow 12$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.129$
$S = 1.05$
4921 reflections
263 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 0.69P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.41$ e Å^{-3}

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C3—H3$\cdots$N23^{ii}	0.95	2.62	3.4682 (19)	149
O1—H1$\cdots$N27	0.84	2.60	3.2292 (17)	133
O1—H1$\cdots$N28	0.84	1.87	2.6846 (18)	162
C5*P*—H5*P*$\cdots$N27^{i}	0.95	2.81	3.750 (2)	169

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

All H atoms were placed in calculated positions and refined using a riding model [C—H(aryl) = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$; C—H(tertiary alkyl) = 1.00 Å and $U_{iso}(H) = 1.2U_{eq}(C)$; C—H(methyl) = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$; and O—H = 0.84 Å and $U_{iso}(H) = 1.2U_{eq}(O)$].

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: local program.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1606). Services for accessing these data are described at the back of the journal.

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