

## 1,1'-Bis(2-nitrophenyl)-5,5'-dipropyl-3,3'-bipyrazole

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## Key indicators

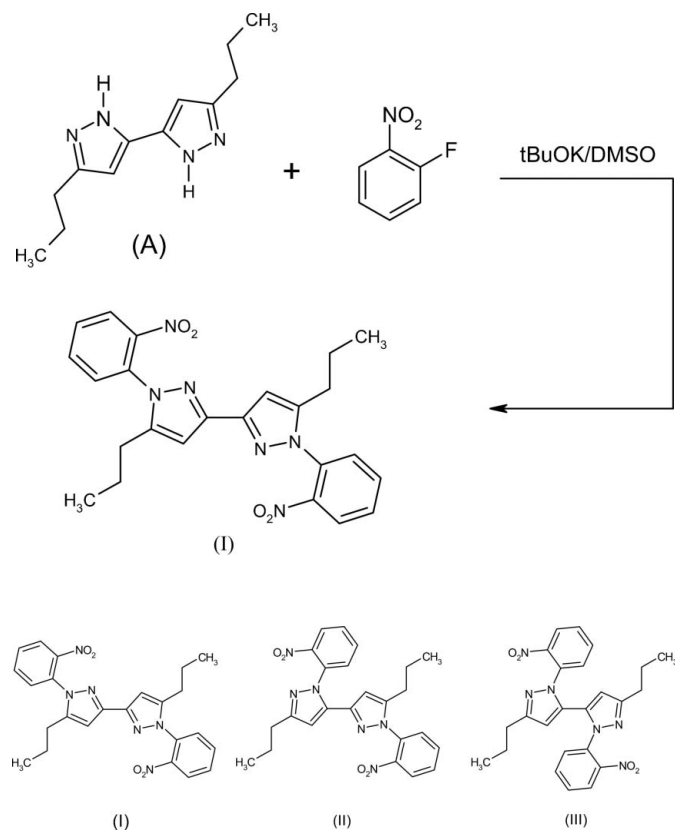
Single-crystal X-ray study  
 $T = 173\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$   
 $R$  factor = 0.076  
 $wR$  factor = 0.126  
Data-to-parameter ratio = 8.3For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.In the title compound,  $\text{C}_{24}\text{H}_{24}\text{N}_6\text{O}_4$ , the two pyrazole rings are essentially coplanar, with a dihedral angle of  $2.8(3)^\circ$ .Received 26 October 2005  
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## Comment

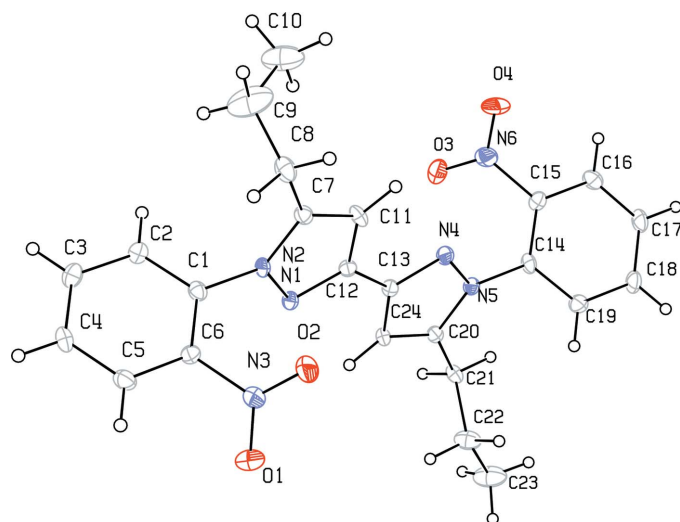
Five-membered N-heterocycles have been studied as models of simple aromatic systems; some of them are of great biological and pharmaceutical interest, and pyrazole has often been at the centre of such research (Tarimci & Schempp, 1977). 2,2'-Bipyridine is the most widely used chelate system (Kaes *et al.*, 2000) for mononuclear (Balzani *et al.*, 1978; Kalyanasundram, 1992) and polynuclear transition metal complexes used in the field of luminescence (Balzani *et al.*, 1996; Ward *et al.*, 1998), photonics and optoelectronics (Venturi *et al.*, 1999). Owing to the similarity of their molecular structures with that of 2,2'-bipyridine, we believe that new 3,3'-bipyrazole derivatives deserve to be prepared and studied. The well documented bio-activity of pyrazole derivatives (isomeric with imidazoles) is often related to chelation phenomena (Skipper *et al.*, 1957) with trace metal ions; this has generated substantial work on the coordination chemistry of pyrazole-derived ligands, widely described by Trofimenko in a series of review articles (Trofimenko, 1972, 1986, 1993). Bipyrazolyl derivatives have proven to be useful as potential anti-inflammatory agents (Bruno *et al.*, 1993), cytotoxic agents (Cuadro *et al.*, 1985), insecticides (Tsuboi *et al.*, 1994), herbicides (Hartfiel *et al.*, 1993) and fungicides (Desbordes *et al.*, 1994). C,C-linked bipyrazole derivatives are also used in the photographic and paint industries (Allen *et al.*, 1963). The reaction of 3,3'-dichloro-5,5'-bipyrazole with  $\text{Ni}(0)L_m$  gives new poly(bipyrazoles) with high thermal stability (Murakami *et al.*, 1999), while the palladium(II) and platinum(II) complexes of 5,5'-dimethyl-3,3'-bipyrazole display anti-tumour properties (Saha & Misra, 1995). Crystal structures of 1-(4-nitrophenyl)pyrrole, -imidazole, -pyrazole and -1,2,3-triazole derivatives have been determined to assess the non-linear optical properties of crystals (Ishihara *et al.*, 1992) and a series of compounds was prepared to explore new non-linear optical materials with high transparencies for blue light (Okazaki *et al.*, 1987).

In this paper, we describe the preparation and the crystal structure of the new 1,1'-di(2-nitrophenyl)-5,5'-dipropyl-3,3'-bipyrazole, (I). It has been prepared by a regioselective *N*-arylation reaction of 3,3'-dipropyl-5,5'-bipyrazole (A) with 2-fluoronitrobenzene (see scheme). 3,3'-Dipropyl-5,5'-bipyrazole (A) is an ambidentate nucleophile with a nucleophilic centre not localized at an N atom; in fact, both N atoms of each pyrazole ring can be arylated to provide a mixture of three regioisomers, (I), (II) and (III). The molecular structure of product (I) was determined using IR, MS and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies. To confirm the positions where the propyl and

nitrophenyl groups are attached to the 3,3'-bipyrazole ring system and to obtain more detailed information on the molecular conformation and packing in the solid state, the X-ray crystal structure determination of (I) has been carried out.



Although the two 1-(2-nitrophenyl)-5-propylpyrazole moieties in the molecule of (I) are chemically equivalent, they are crystallographically independent. The molecular structure of (I) is shown in Fig. 1. The C7—C8 and C20—C21 bond lengths of 1.482 (5) and 1.493 (5) Å, respectively, are considerably shorter than the methyl-phenyl bond of 1.52 Å in toluene (Sutton, 1965), but they compare well with bonds between the pyrazole ring and the methyl group in 1-(*p*-nitrophenyl)-3-methyl-4-bromopyrazole (Lapasset & Falgueirette, 1972). As shown by the maximum deviations of atoms from the calculated least-squares plane, 0.028 (9) Å and −0.019 (9) Å for C24 and C7, respectively, the two 5-membered *N*-heteroatomic rings are essentially coplanar; the maximum deviation is 0.012 Å for atom C6 of pyrazole in 1-(*p*-nitrophenyl)-3-methyl-4-bromopyrazole (Lapasset & Falgueirette, 1972). The geometry of the nitro group, and also the C—N bond length, are very similar to literature reports: 1.466 (5) and 1.461 (5) Å for C—N bonds in 4-bromo-3-methyl-1-(4-nitrophenyl)-1*H*-pyrazole (Lapasset & Falgueirette, 1972), ranging from 1.47 to 1.48 Å in other nitrophenyl pyrazoles (Lapasset & Falgueirette, 1972) and 1.478 (13) Å in *o*-nitrobenzoic acid (Tavale & Pant, 1973). The N—O bond lengths, ranging from 1.201 (4) to 1.227 (4) Å, are comparable with the values quoted for similar nitro-substituted



**Figure 1**  
The molecular structure of (I), with displacement ellipsoids drawn at the 30% probability level.

compounds: tri-*p*-nitrophenyl phosphate (Mazhar-ul-Haque & Caughlan, 1970), 1.22 (1) Å; *o*-nitrobenzoic acid, 1.20 (1) and 1.22 (1) Å. Around atoms N3 and N6, the C—N—O angles, from 116.6 (4) to 119.2 (4)°, and the O—N—O angles of 124.2 (4) and 123.8 (4)°, are not significantly different from those found in *o*-nitrobenzoic acid and 1-(2',4'-dinitrophenyl)-4-chloropyrazole (Sutherland *et al.*, 1974). As already reported for *p*-dinitrobenzene (Di Rienzo & Riva di Sanseverino, 1980), atom C6, to which the nitro group is attached, is slightly (0.055 Å) out of the plane defined by atoms O1, O2 and N3. The torsion angles of 48.4 (3) and 49.4 (2)° between the nitro groups and the benzene rings to which they are attached indicate a very weak conjugation of the NO<sub>2</sub> group with the aromatic ring. In compound (I), with an N1—C12—C13—N4 torsion angle of −179.1 (3)°, the two pyrazole heterocycles are coplanar, as also observed for 3,3'-bipyrazole (Monge *et al.*, 1994). However, other *C,C*-linked bipyrazoles display completely different conformations, for example 3,3'-dichloro-4,4'-bis(methoxycarbonyl)-1,1'-dimethyl-5,5'-bipyrazole (Murakami & Yamamoto, 1999) and 1-phenyl-3-methyl-4(1-phenyl-3-methyl-1*H*-pyrazol-5-yl)-2*H*-3-pyrazolin-5-one (Kumar *et al.*, 1995), with respective torsion angles of 107.0 (6) and −119.1 (7)° which result from steric strain. Note the torsion angles of 51.1 (4) and 73.9 (3)° between the pyrazole and benzene rings in (I), reflecting some steric repulsion between the propyl and nitrophenyl substituents of each pyrazole ring.

## Experimental

To a solution of 5,5'-dipropyl-3,3'-bipyrazole (0.5 mmol) in dimethyl sulfoxide (2 ml) was added solid potassium *tert*-butoxide (1.1 mmol), followed by 2-fluoronitrobenzene (1.05 mmol) in dimethyl sulfoxide (1 ml) through a syringe. The resulting mixture was heated to 343 K and kept at this temperature for 2 h. The mixture was cooled to room temperature and quenched with water (10 ml). Compound (I) was collected by filtration and oven-dried under a vacuum. Single crystals

were obtained by recrystallization from a mixture of EtOH and CH<sub>2</sub>Cl<sub>2</sub> (9:1 v/v).

#### Crystal data

C <sub>24</sub> H <sub>24</sub> N <sub>6</sub> O <sub>4</sub>	Mo K $\alpha$ radiation
$M_r = 460.49$	Cell parameters from 4517 reflections
Orthorhombic, $P2_12_12_1$	$\theta = 2.9\text{--}26.2^\circ$
$a = 7.720$ (1) Å	$\mu = 0.10$ mm <sup>-1</sup>
$b = 16.200$ (2) Å	$T = 173$ (2) K
$c = 18.058$ (2) Å	Parallelepiped, yellow
$V = 2258.5$ (5) Å <sup>3</sup>	$0.49 \times 0.20 \times 0.06$ mm
$Z = 4$	
$D_x = 1.354$ Mg m <sup>-3</sup>	

#### Data collection

Oxford Diffraction Xcalibur CCD diffractometer	2187 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.11$
Absorption correction: none	$\theta_{\text{max}} = 26.2^\circ$
33955 measured reflections	$h = -9 \rightarrow 9$
2582 independent reflections	$k = -20 \rightarrow 20$
	$l = -22 \rightarrow 22$

#### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.042P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.076$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.36$ e Å <sup>-3</sup>
2582 reflections	$\Delta\rho_{\text{min}} = -0.25$ e Å <sup>-3</sup>
310 parameters	Extinction correction: <i>SHELXL97</i>
H-atom parameters constrained	Extinction coefficient: 0.0055 (9)

**Table 1**

Selected geometric parameters (Å, °).

N3—O2	1.201 (4)	N6—O3	1.227 (4)
N3—O1	1.219 (4)	C7—C8	1.482 (5)
N6—O4	1.222 (4)	C20—C21	1.493 (5)
O2—N3—O1	124.2 (4)	O4—N6—O3	123.8 (4)
O2—N3—C6	119.2 (4)	O4—N6—C15	118.0 (4)
O1—N3—C6	116.6 (4)	O3—N6—C15	118.1 (4)
N1—C12—C13—N4	-179.1 (3)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
C23—H23C $\cdots$ O2 <sup>i</sup>	0.96	2.51	3.352 (6)	146
C18—H18 $\cdots$ O3 <sup>ii</sup>	0.93	2.48	3.212 (5)	136
C5—H5 $\cdots$ O1 <sup>iii</sup>	0.93	2.54	3.228 (5)	131

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

All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}$  for other H atoms; C—H distances are 0.93–0.97 Å. No disorder was resolved, despite the relatively large displacement parameters of the propyl groups.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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