

Crystal Structure of N,N,N',N'-tetra-[(3,5-dimethyl-1-pyrazolyl)methyl]-*para*-phenylenediamine

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Abstract: The title compound, molecular formula C₃₀H₄₀N₁₀, crystallizes and exhibits a cisoidal conformation around a central *p*-phenylenediamine ring suggesting that this bis-tripodal ligand is highly flexible and could be accommodated by many and original metal coordinations. All four five-membered pyrazole rings are identical. The molecule presents an inversion centre that coincides with the phenyl ring centre: pyrazole rings are two-by-two equivalent. The electrostatic spatial intramolecular repulsion between N4 and N5 is probably responsible for this general arrangement. These data emphasize the basic character of nitrogens N4 and N5.

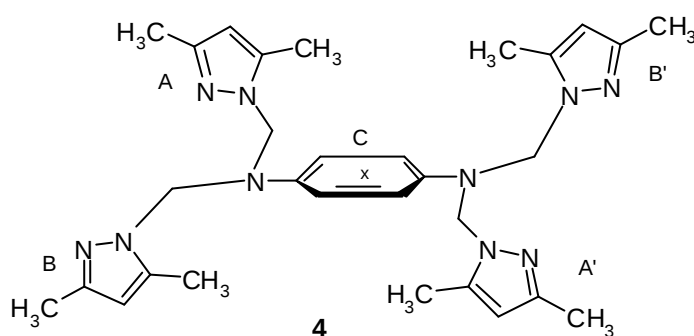
Keywords: Structure, *bis*-tripod, pyrazole, bis-tridentate, N-ligands, condensation, diamines, flexibility, molecular wires.

Introduction

Polydentate pyrazole compounds are known and particularly interesting as promising ligands for the building of polynuclear complexes as models for bioinorganic systems [1] as well as for the discovery of new

catalyst precursors [2]. We are currently working on the synthesis and coordination of mono-tripodal nitrogen ligands, such as N,N-bis-[(3,5-dimethyl-1-pyrazolyl) methyl] alkylamines [3] to gain insight into the coordination behaviour of larger ligand systems containing at the same time nitrogens of pyrazolyl groups as potential N-donor atoms, and a delocalised π -conjugated spacer as aryl diamine. This research effort is directed to the preparation of new mixed valence transition metal complexes for catalysis, with a particular interest in electronic communication [4,5]. The X-ray structure of N,N,N',N'-tetra-[(3,5-dimethyl-1-pyrazolyl)methyl]*para*-phenylenediamine (**4**) (Scheme1) was determined to establish its spatial conformation.

Scheme 1

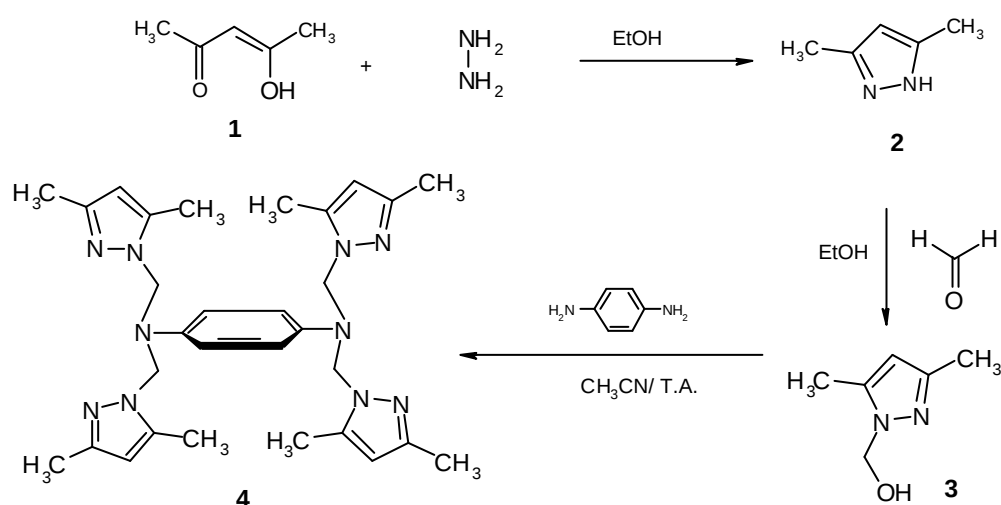


Results and Discussion

Synthesis of bis-tripodal ligand (**4**).

The title compound **4**, which possesses six nitrogen donor sites, was prepared using a modification of the literature method [3, 6-9] (Scheme 2).

Scheme 2

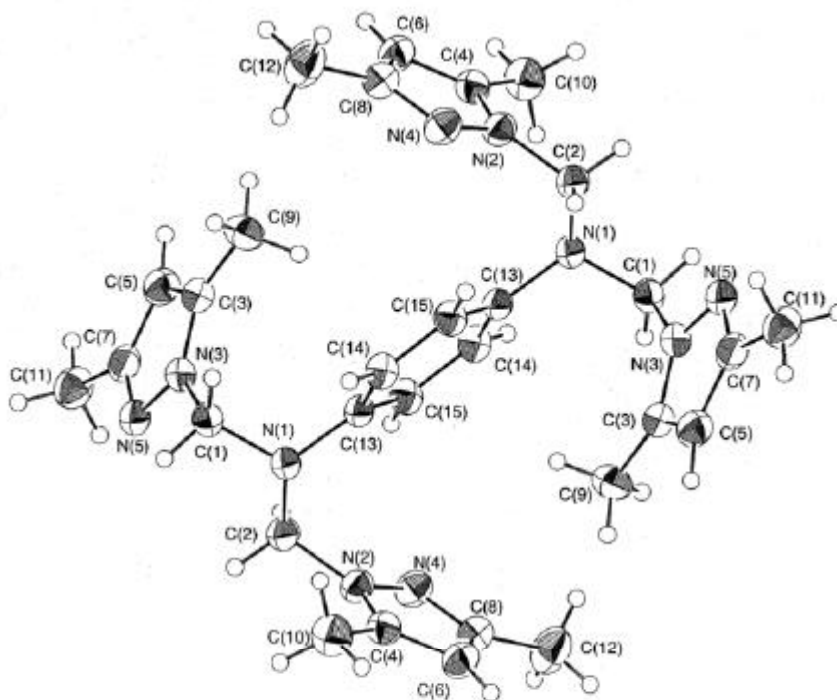


Thus, **4** was easily prepared from the condensation of four equivalents of 1-(hydroxymethyl)-3,5-dimethylpyrazole with one equivalent of *p*-phenylenediamine under gentle conditions (room temperature, atmospheric pressure, 4-7 days), using anhydrous acetonitrile as solvent. The yield was good (67%) and the compound **4** was crystallized from dichloromethane/ether.

Crystallographic study of bis-tripodal ligand (4).

The X-ray data for a crystal of the title molecule **4** were collected with graphite-monochromatized Mo Ka radiation at 298 K. The crystal structure has been deposited at the Cambridge Crystallographic Data Centre [10]. The structure was solved by direct methods and refined by full-matrix least-squares with anisotropic temperature factor, for the non-hydrogen atoms. The hydrogen atoms were localized on difference Fourier map and adjusted to 0.97 Å to bonded atoms. The molecular structure of the title compound is shown in Scheme 3, together with the atomic labelling scheme.

Scheme 3: Molecular structure of the title compound with atom labelling. Thermal ellipsoids are drawn at the 50% probability level.



It presents a cisoid (A/A') and cisoid (B/B') conformation via central phenyl ring (C). All four five-membered pyrazole rings are identical. The molecule **4** has an inversion centre *x* which coincides with the phenyl ring centre's (C) (Scheme 3). So the pyrazole rings A and A' are symmetrically related. The same observation is available for the second rings pair (B and B'). The electrostatic spatial intermolecular repulsion between N4 and N5 is probably responsible of this general (A/A'-B/B') disposition. These data led us to note the nitrogen's basic character of N4 and N5. The N1-C1 bond length is 1.441(2) Å. It is slightly greater than

those of other similar rings; for example 3-formyl-5-methylpyrazolyl group, with about 1.361(2) Å [11] probably suggesting that 3,5-dimethylpyrazolyl group of compound **4** is more conjugated. The same observation is valid for the N=N bonds; for example, the N2=N4 bond length is 1.368(2) in **4**; the same N=N bond length in the 3-formyl-5-methylpyrazolyl group is 1.346(2) Å [11].

Thus the molecule consists of four structurally analogous (3,5-dimethylpyrazol-1-ylmethyl) units, adopting a cisoidal conformation via a central *p*-phenylenediamine ring, suggesting that this bis-tripodal ligand is highly flexible and could be accommodated to many and original metal coordinations. Table 1 summarises the crystal and experimental data.

Table 1 Crystal and experimental data of *bis*-tripod **4**

Formula: C ₃₀ H ₄₀ N ₁₀	
Formula weight = 540.43	
Crystal system: monoclinic	
Space group: P2 ₁ /a	Z = 2
a = 11.262(2) Å	α = 90.00 (1) °
b = 12.259(3) Å	β = 109.8 (8) °
c = 11.876(5) Å	γ = 90.00 (1) °
V = 1517.6(5) Å ³	
D _x = 1.183 g/cm ³	
μ (Mo K _α) = 0.8 cm ⁻¹	
Shape = near prismatic form 0.16, 0.17, 0.20 mm	
Transmission min = 0.691	
Transmission max = 1.036	
T = 298K	
F (000) = 580	
Radiation: Mo K _α 0.71073	
θ _{max} = 29.98 °	
R = 0.045 (on F)	
R _w = 0.093 (on F ²)	
(ΔP) _{max} = +0.54	
(ΔP) _{min} = -0.47	
No. of reflections measured = 4622	
No. of reflections used = 1509	
No. of parameters = 182	
Goodness-of-fit = 0.551	
Measurement- Kappa CCD – Nonius Diffractometer	
Program system: MaXus	

Absorption correction : Sortav

Molecular Graphics : ORTEP

The structure refinement has been carried out with the appropriate by crystallography programs [12-16].

Conclusions

We have explored the easy synthesis of tridentate pyrazolic derivatives ligands to establish the structure of one bis-tripod of this class. We are now examining if this bis-tripodal class could display some biological activity and we are now extending this synthesis to some bis-tripodal transition metal complexes which are suitable organometallic models of molecular wires.

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Experimental

General

Melting points were measured on an Electrothermal apparatus and are uncorrected, proton NMR spectra of the compound **4** dissolved in CDCl_3 , was obtained with an AC 250 MHz Bruker spectrometer. Reagents and solvents were purchased from commercial suppliers.

Preparation of *N,N,N',N'*-tetra-[(3,5-dimethyl-1-pyrazolyl) methyl]para-phenylenediamine (**4**).

Compound **4** was prepared by the addition of *p*-phenylenediamine ($\text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{NH}_2$) to the substituted hydroxymethylpyrazole **3** [1] according to the modified procedures [3,7-10]. To a solution of **3** (2.52 g, 20 mmol) in acetonitrile (40 mL) was added *p*-phenylenediamine (0.54 g, 5 mmol) and the mixture was stirred at 20 °C for a week. The residue was precipitated by addition of cold water, purified and washed with hexane and then dried under vacuum, to afford **4** as a pure white solid (1.8 g, yield = 67%), which was recrystallized from dichloromethane / ether; M.p. 174-176°C. IR (KBr, cm^{-1}): 2980 (CH), 1590 (C=C), 1490 (C=N), 1430, 1320, 1280, 1220, 1170, 1080, 1040, 910, 840, 790; ^1H -NMR (250 MHz, CDCl_3) δ ppm: 7 (s, 4H, $-\text{C}_6\text{H}_4-$), 5.8 (s, 4H, Pyrazolyl- C^4), 5.5 (s, 8H, NCH_2N), 2.3 (s, 12H, Pyrazol- CH_3), 2 (s, 12H, Pyrazol- CH_3). MS [FAB; MeOH/GLY] (Calc. for $[\text{M}]^+ \text{C}_{30} \text{H}_{40} \text{N}_{10}$: 540); Found $[\text{M}]^+$ (m/z): 540. , m/z = 445

$[\text{C}_5\text{H}_8\text{N}_2]^+$, $m/z = 241$ $[\text{C}_{14}\text{H}_{17}\text{N}_4]^+$. Elemental Analysis for $\text{C}_{30}\text{H}_{40}\text{N}_{10}$ Cal. (Found): C 66.66 (65.82); H 7.4 (6.98); N 25.9 (25.24%).

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- 10 CCDC 186572 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via the URL <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).
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Sample Availability: Samples of compound **4** are available from the authors and MDPI.