# Synthesis, characterisation and crystal structure of a new bis-tripodal ligand: *N,N,N′,N′*-tetrakis[(1,5-dimethylpyrazol-3-yl)methyl]-1,4-phenylenediamine

**Ibrahim Bouabdallah[a], Abdelkrim Ramdani[a], Ismail Zidane[a], Rachid Touzani[a], Driss Eddike[b], Smaail Radi[a]* and Abel Haidoux[c]**

[a]*Laboratoire de Chimie Organique Physique, Département de Chimie, Faculté des Sciences, Université Mohamed I, Oujda, Marocco*

[b]*Laboratory of Inorganic Solid State Chemistry, Department of Chemistry, Oujda, Marocco*

[c]*Laboratoire de physicochimie de la matière condensée, Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier, France*

The synthesis of a new bis-tripodal ligand *N,N,N′,N′*-tetrakis[(1,5-dimethylpyrazol-3-yl)methyl]-1,4-phenylenediamine is reported and clearly established from its spectroscopic data (IR, $^1$H NMR, mass spectrometry) and elemental analysis. The X-ray structure of the target compound has been determined and the pyrazolyl ligand crystallises in the space group P-1 [$C_{30}H_{40}N_{10}$; $a$ = 7.1533(7)Å; $b$ = 9.7541(10)Å; $c$ = 10.7169(10)Å; α = 94.420(8)°; β = 97.920(8)°; γ = 108.088(9)°, Z = 2].

**Keywords:** synthesis, pyrazole, N-ligand, bis-tripod, structure, conformation

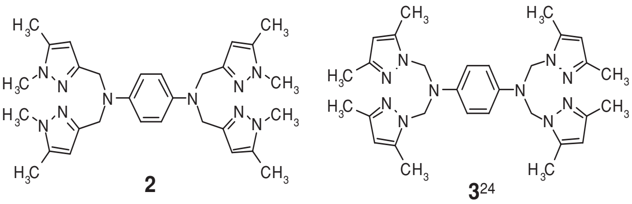
There is considerable interest in the synthesis of multidentate organic ligands for the building of polynuclear complexes as potential models for biological dimetallic sites[1-7] as well as for the catalytic systems in synthetic processus.[8] Polypyrazolyl containing ligands are used in models for copper proteins to mimic active sites.[9-11] Tris-pyrazolyl borates are bulky ligands in metal complexes and have been adapted for the discovery of new activation processes and new catalytic reactions.[12-14] Moreover, a variety of nitrogen containing polydentate ligands is able to promote novel catalytic transformations of organic substrates,[15] including enantioselective catalysis[16] and alkenes polymerisation.[17] Several *N,N*-bis(pyrazolyl-1-methyl) amines have already been described.[18] These compounds were characterised by N–C–N bonds.

As part of our research program investigating bis- and tetra-pyrazolyl ligands, we have focused attention on bis-tripod ligand in order to synthesise homo- or hetero-binuclear complexes. This research effort is directed to the preparation of new bimetallic complexes for catalysis and intramolecular electron transfer.[19-23]

We now report the synthesis of a new pyrazolyl ligand *N,N,N′,N′*-tetrakis[(1,5-dimethylpyrazol-3-yl)methyl]-1,4-phenylenediamine **2** (Fig. 1) in which the pyrazole rings are linked to the benzene ring by C–C–N junctions, steadier than its isomer *N,N,N′,N′*-tetrakis -[(3,5-dimethylpyrazol-1-yl) methyl]-1,4-phenylenediamine **3**[24] in which the pyrazoles are linked to the benzene ring by N–C–N junctions.[18,20,25,26] The X-ray structure of **2** was determined to establish its spatial conformation in the free state before coordination to metals.

## Results and discussion

Our strategy was to develop a simple and convenient method for obtaining the bis-tripod ligand. The result of our investigation is given below (Scheme 1). The bis-tripod ligand **2** has been synthesised according to the method used in our laboratory.[27-31] The condensation of the known 3-chloromethyl-1,5-dimethylpyrazol **1** with *p*-phenylenediamine in ratio 4:1, using sodium carbonate as base yielded after 3 h of reflux one isolated major product **2** in 55% yield which was recrystallised from ethanol. In view of the size of this molecule, one might expect it to have a complex NMR spectrum. However, this is, in fact, extremely simple. $^1$H NMR spectrum of this molecule in $CDCl_3$ solution shows two methyl signals which appears at 2.16 ppm and 3.67 ppm corresponding to C–$CH_3$ and N–$CH_3$ protons respectively. The C-4 protons show one peak at 5.91 ppm, the methylene protons a signal at 4.35 ppm and the benzene ring protons a signal at 6.81 ppm. This spectrum indicates that the molecule has a considerable symmetry. The IR spectra shows the band at 1520 cm$^{-1}$ corresponding to the vibration of C=N and C=C of the pyrazole and benzene rings. The mass spectrum displayed a molecular ion peak at *m/z* 540 (70%). The proposed fragmentation of this new bis-tripod ligand is illustrated in Scheme 2.



**2** **3**[24]

**Fig. 1** Structures of a new bis-tripod **2** and a literature compound **3**.

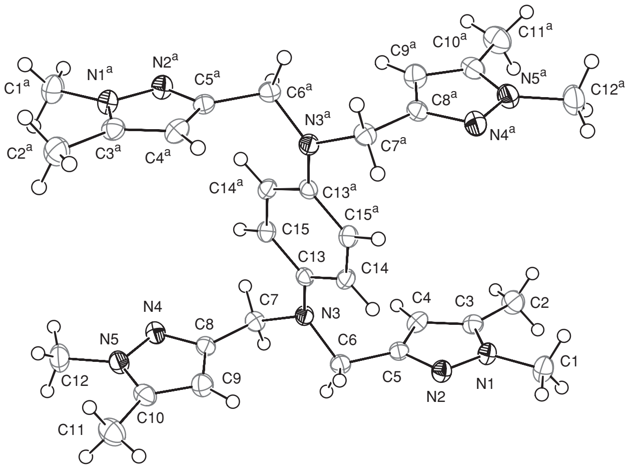


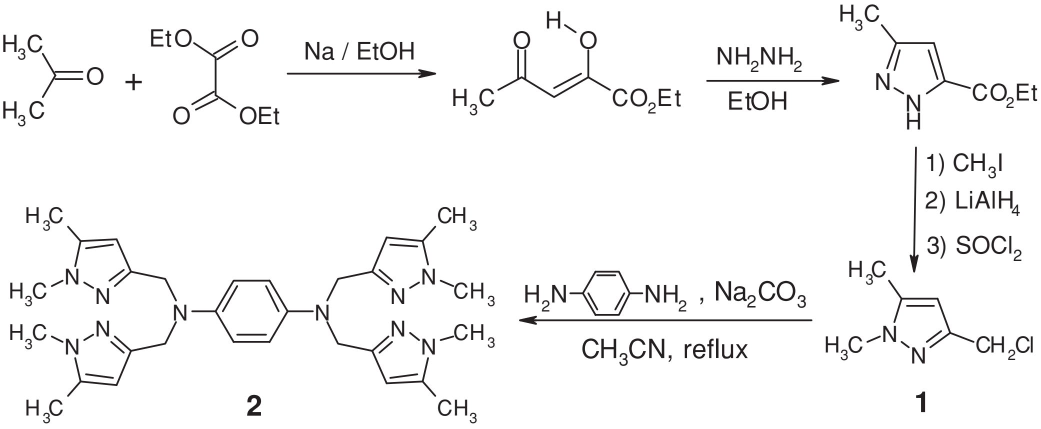
**Fig. 2** Molecular structure of **2** with the atom-numbering scheme.

## Crystal structure

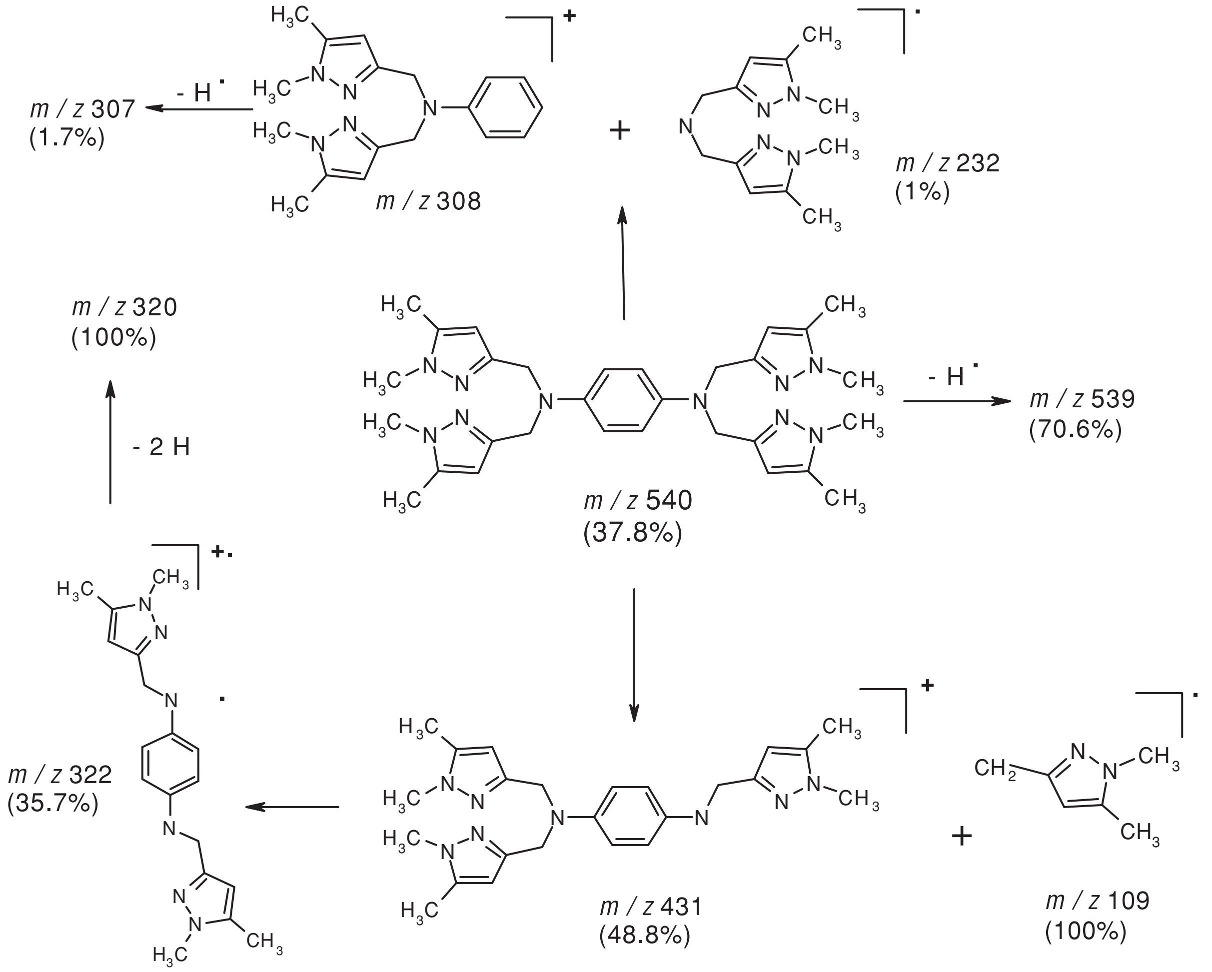
The internal and external angles of the pyrazole ring follow the set of empirical rules given by Bonati and Bovio,[32] such that

---

* Correspondent. E-mail: Radi@sciences.univ-oujda.ac.ma



Scheme 1



Scheme 2

(a) N1N2C5 (104.65) is smaller than N2–N1–C3 (112.42); (b) N2C5C4 (111.02) is larger than N1N2C5 (104.65), C5C4C3 (106.17) and N1C3C4 (104.74); (c) C5C4C3 (106.17) is not the largest internal angle; (d) N2N1C1(119.66) is smaller than C3–N1–C1(127.92); (e) H(C4)–C4–C5 (126.9) and H(C4)–C4–C3 are equal. The C4–C3 (1.376) distance is shorter than C5–C4 as expected in neutral pyrazole rings.[33]

The conformations of bis-tripod ligand 2 and its similar structure isomer **3**[24] in which the pyrazole is linked to the benzene ring by an N–C–N junction are completely different. Indeed, In the title of compound **2**, the pyrazole rings are quasi-coplanar (dihedral angle of 7.71°), while in **3** the two heterocycles are approximately orthogonal with a dihedral angle of 87.88(12). The dihedral angle between the pyrazolic rings and the benzene ring is also different in the two isomers: 84.66 and 79.77 in the bis-tripod **2** and 50.40 (17) and 72.05 (17) for **3**.

The angles around the aniline N diverge from ideal tetrahedral values and the comparison between **2** and **3** shows some differences such that angles C13N3C7 of 119.01(12) and C13N3C6 of 118.30 in **2** are larger than C13N1C1 of 114.6(8) and C13N1C2 of 117.4 in **3**. The distance N3

**Table 1**

| Bond distances/Å | Angles/° |
|---|---|
| 1.398(5) | 116.8(4) – 121.3(4) – 121.3(4)[34] |
| 1.4069(18) | 116.45 – 118.30 – 119.01 (ligand **2**) |
| 1.428(3) | 116.4(2) – 118.5(2) – 115.1(2)[35] |
| 1.447(4) | 114.1(8) – 114.6(8) – 117.4(8) (ligand **3**[24]) |
| 1.456(7) | 113.2(5) – 113.7(5) – 113.5(5)[35] |

C13 of 1.4067 in **2** is shorter than in **3** (C13N1: 1.447). The explanation makes use of the idea that the aniline nitrogen can participate in the multicentre bonding of the benzene ring by donating electrons to it. As we can see in Table 1, because of the steric strain between the groups linked to the aniline N, when the value of the angles around the aniline N is greater the distance N–C becomes shorter and the hybridisation of N becomes closer to $sp^2$ hybridisation.

## Conclusion

The new ligand *N,N,N',N'*-tetrakis[(1,5-dimethylpyrazol-3-yl) methyl]-1,4-phenylenediamine in which the junctions are very strong than those of its isomer offers the possibility to form new di-nuclear complexes. The present study shows that the nature of the junction between the benzene and the pyrazolic rings considerably changes the molecular geometric and consequently the nature of the complex obtained.

## Experimental

Melting points uncorrected were determined on BUCHI 150 Melting Point apparatus. The IR spectra were taken with potassium bromide discs on Perkin Elmer 1310 spectrometer. $^1$H NMR spectra was recorded on a Bruker 300 spectrometer (operating at 300.13 MHz). Chemical shifts are listed in ppm and are reported relative to tetramethylsilane. Mass spectra were obtained on a VG7070E spectrometer.

*Synthesis of N,N,N',*N'-tetrakis[(1,5-dimethylpyrazol-3-yl)methyl]-1,4-phenylenediamine **2**. A mixture of *p*-phenylenediamine (54 mg, 0.50 mmol), 3-chloromethyl-1,5-dimethylpyrazol **1** (288 mg, 2 mmol) and sodium carbonate (414 mg, 4 mmol) in anhydrous acetonitrile (6 ml), was refluxed for 3 h. After filtration, the solvent was concentrated at reduced pressure. The residue was purified by recrystallisation from ethanol to afford the product **2** as a white solid. Rf = 0.32 ($CH_2Cl_2$ / EtOH, 95:5); Yield: 150 mg, 55 %; Melting point: 184–185 °C (EtOH); IR (KBr, cm$^{-1}$): ν(C–H)ar = 3050, ν($CH_3$) ar = 2940, ν(C–H, N–$CH_3$)= 2880, ν(C=C, C=N) = 1520, $\delta_s$ ($CH_3$) = 1370–1380; $^1$H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.81 (4H, C–H ph); 5.91 (s, 4H, C–H pz); 4.35 (s, 8H, $CH_2$); 3.67 (s, 12H, N–$CH_3$); 2.16 (s, 12H, pz-$CH_3$). Anal. Calc. for $C_{30}H_{40}N_{10}$: C 66.66, H 7.41, N 25.92, Found: C 66.69, H 7.45, N 25.86 *m/z*: 540 ($M^+$).

*Crystal structure determination:* On a bulk synthesised, some crystals were selected and checked for singularity by preliminary oscillation and Weissenberg photographs.

The best diffractant crystal was used for intensity measurements on a CCD diffractometer (Xcalibur, Oxford Diffraction), it displays the triclinic system, space group P-1, with parameters $a$ = 7.1533(7)Å, $b$ = 9.7541(10)Å and $c$ = 10.7169(10)Å, α = 94.420(8)°, β = 97.920(8)° and γ = 108.088(9)°.

The crystal structure solution was carried out with shelxS-97 using directs methods and some atoms are located. The structure completion was performed with shelxL-97 using Fourier and Difference Fourier synthesis. The recorded frames, with theta max of 32.33 degree gave a total of 13718 reflections of which 4446 were unique and 2565 observed. Atomic positions and thermal parameters reafinements were done using the full matrix least squares method.

Hydrogen atoms were placed in geometrically idealised positions and constrained to ride on their parent atoms with Uiso(H) = 1.5 Ueq(C) for methyl groups and 1.2Ueq(C) for others.

The final agreement index or reliability factorR1 is 0.0601.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 254829. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

*Received 7 December 2004; accepted 26 January 2005*
*Paper 04/2921*

## References

1 N.J. Blackburn, R.W. Strange, A. Farooq, M.S. Haka and K.D. Karlin, *J. Am. Chem. Soc.,* 1988, **110**, 4263.
2 K.D. Karlin, P. Ghosh, R.W. Cruse, A. Farooq, Y. Gultneh, R.R. Jacobson, N.J. Blackburn, R.W. Strange and J. Zubieta, *J. Am. Chem. Soc.*, 1988, **110**, 6769.
3 N. Kitajima, T. Koda, S. Haschimoto, T. Kitagawa and Y. Morooka, *J. Am. Chem. Soc.*, 1991, **113**, 5664.
4 T.N. Sorrell, M.L. Garrity and D.J. Ellis, *Inorg. Chim. Acta.*, 1989, **166**, 71.
5 T.N. Sorrell and V.A. Vankai, *Inorg. Chem.*, 1990, **29**, 1687.
6 T.N. Sorrell, V.A. Vankai and M.L. Garrity, *Inorg. Chem.*,1991, **30**, 207.
7 F.C.G.M. Van Veggel, S. Harkema, M. Bos, W. Verboom and D.N. Reinhoudt, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 746.
8 T. Kawato, H. Koyama, H. Kanatomi and Y. Muramoto, *Inorg. Chim. Acta*, 1991, **183**, 107.
9 T.N. Sorrell, D.L. Jameson and C.J. O'Connor, *Inorg. Chem.*, 1984, **23**, 190.
10 T.N. Sorrell, C.C. Shen and C.J. O'Connor, *Inorg. Chem.*, 1987, **26**, 1755.
11 P.P. Paul, Z. Tyeklar, R.R. Jacobson and K.D. Karlin, *J. Am. Chem. Soc.*, 1991, **113**, 5322.
12 C. Slugove, K. Mauthner, M. Kacetl, K. Meriter, R. Schmid and K. Kirchner, *Chem. Eur. J.,* 1998, **4**, 2043.
13 S. Trofimenko, *Chem. Rev.,* 1993, **93**, 943.
14 N. Kitajima and Y. Moro-oka, *Chem. Rev*., 1994, **94**, 737.
15 S. Kobayashi, H. Uchiro, Y. Fujishita, I. Shiina and T. Mukaiyama, *J. Am. Chem. Soc.* 1991, **113**, 4247.
16 D. Muller, G. Umbreeht, B. Weber and A. Pfaltz, *Helv. Chim. Acta,* 1991, **74**, 722.
17 L.K. Johnson, C.M. Killian and M.S. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414.
18 W.L. Driessen, *J. Royal Netherlands Chem. Soc.,* 1982, **101**, 441.
19 J.P. Launay, *Chem. Soc. Rev.,* 2001, **30**, 386.
20 K.D. Demadis, C.M. Hartshorn and T.J. Meyer, *Chem. Rev.*, 2001, **101**, 2655.
21 B.S. Brunschwig, C. Creutz and N. Sutin, *Chem. Soc. Rev.,* 2002, **31**, 168.
22 E. Sondaz, J. Jaud, J.P. Launay and J. Bonvoisin, *Eur. J. Inorg. Chem*., 2002, **8**, 1924.
23 P. Karafiloglou and J.P. Launay, *Chem. Phys*., 2003, **289**, 231.
24 M. Daoudi, N. Ben Larbi, D. Benjelloun, A. Kerbal, J.P. Launay, J. Bonvoisin, J. Jaud, M. Mimouni and T. Ben-Hadda, *Molecules*, 2003, **8**, 269.
25 W.L. Driessen, W. Wiesmeijer, R.A.G. De Graaff, M. Schipper-Zablotskaja and J. Reedijk, *Inorg. Chim. Acta,* 1989, **162**, 233.
26 B. Barszcz, T. Glowiak, J. Jezierska and K. Kurdziel, *Inorg. Chem. Commun.*, 2002, **5**, 1056.
27 S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini, J. Morcellet and L. Janus, *Eur. Polym. J*., 2000, **36**, 1885.
28 S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini and L. Janus, *Tetrahedron*, 2004, **60**, 939.
29 S. Radi, A. Ramdani, Y. Lekchiri, M. Morcellet, G. Crini and L. Janus, *J. Chem. Res*., 2003, **11**, 712.
30 F. Malek, M. Persin, A. Ramdani, J. Sarrazin and I. Zidane, *New J. Chem*., 2002, **26**, 876.
31 F. Malek, A. Ramdani and S. Radi, *J. Chem. Res*., 2004, **9**, 640.
32 F. Bonati and B. Bovio, *J. Spectrosc. Res.,* 1990, **20**, 233.
33 S.J. Zukerman, E.E. Castellano, G. Olivia, A.C. Massabni and A.D. Pinto, *Can. J. Chem*., 1984, **2**, 725.
34 M. Daoudi, N. Ben Larbi, D. Benjelloun, A. Kerbal, J.P. Launay, J. Bonvoisin, J. Jaud, M. Mimouni and T. Ben-Hadda, *Molecules*, 2002, **7**, 690.
35 H.L. Blonk, W.L. Driessen and J. Reedijk, *J. Chem. Soc. Dalton Trans.*, 1985, 1699.