Research Article

Synthesis and Crystal Structure of C_1 -Symmetric 3,3'-Bi(1,1'-dinaphthyl-camphopyrazole)

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The compound 3,3'-bi(1,1'-dinaphthyl-camphopyrazole) **1**, $C_{42}H_{42}O_4$, was obtained in good yield and structurally characterized by 1H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray diffraction. It consists of a 3,3'-bipyrazole group with each pyrazole ring containing a fused camphor group and a naphthalene ring bonded to the adjacent nitrogen atom in the ring. Both of the trimethyl, 5-membered rings of the fused camphor group form an envelope with the apex carbon atom as the flap in each case. In the crystal, weak π - π stacking interactions are observed between nearby 6-carbon rings of the two naphthalene rings linking the molecules into extended chains. Weak π -ring intermolecular interactions are also observed between naphthalene atoms and pyrazole rings from each of the groups helping to stabilize the crystal packing. No classical hydrogen interactions are formed.

1. Introduction

During the last decade, a series of pyrazole-based ligands have been used for catalytic applications [1–3]. However, chiral pyrazole ligands derived from camphor coordinated to transition metals and the catalytic applications of the latter have been less explored [4]. Recently, chiral 3,3'-bipyrazole compounds have been proposed as important ligands that exert electronic and steric stronger influence to the metal center [5, 6]. These ligands were prepared by condensation reaction between a bis-1,3-diketone previously reported [7, 8] and hydrazine hydrate, followed by aryl- or alkylation. Herein, we report the crystal structure of a C_1 -symmetric 3,3'-bi(1,1'-dinaphthyl-camphopyrazole) **1** obtained by direct condensation with α -naphthylhydrazine, which could have an even greater steric effect than the similar ligands previously reported in the literature.

2. Materials and Methods

2.1. General Remarks. 1H and ^{13}C NMR spectra were recorded on a Jeol 400 MHz spectrometer at 25°C with solvent signals allotted as internal standards. Melting point was

determined on an Electrothermal Mel-Temp apparatus in open capillary tubes and is not corrected. CHN elemental analyses were performed on a Fisons EA 1108 analyzer and samples were air handled. Optical rotations were measured on a Perkin-Elmer 341 polarimeter.

2.2. Preparation of 3,3'-Bi(1,1'-dinaphthyl-camphopyrazole)
[Systematic Name: (1,1'-Dinaphthyl-7,7',8,8',8'-hexamethyl-4,4',5,5',6,6',7,7'-octahydro-3,3'-bi-4,7-methano-indazole)] **1**. (1R,1'R)-3,3'-(1,2-Dihydroxyethane-1,2-di-ylidene)bis[1,7,7-trimethylbicyclo[2, 2, 1]-heptan-2-one] (prepared using a modified procedure reported [7]) (0.69 g, 1.95 mmol) and α -naphthylhydrazine hydrochloride (prepared using a modification of the reported procedure [9]) (1.14 g, 5.84 mmol) were suspended in ethanol (50.0 mL). The resulting mixture was heated to reflux for 24 hours. Then, this mixture was neutralized with a saturated solution of Na_2CO_3 . The solid obtained was filtered and washed with chloroform (2×15.0 mL). The solvent was removed under vacuum to obtain the desired product **1** as a white solid (0.58 g, 49%). Mp: $(326 \pm 2)^\circ C$. Elemental analysis is calculated for $C_{42}H_{42}N_4 \cdot 0.4H_2O$: C 82.69%, H 7.07%, N 9.18%. Found: C 82.80%, H 7.26%, N 9.00%. $[\alpha]_D^{20} = +139.3^\circ$

SCHEME 1: Synthesis of 3,3'-bi(1,1'-dinaphthyl-camphopyrazole) **1**.

(c 1.008, CHCl_3). IR (KBr) (ν , cm^{-1}): 3055 (w), 2954 (m), 2870 (w), 1598 (m), 1422 (m), 1388 (m), 1041 (m), 804 (s), 774 (s), 667.69 (w). ^1H NMR (CDCl_3): δ = 0.71 (s, 3H, CH_3), 0.89 (s, 3H, CH_3), 0.97 (s, 3H, CH_3), 1.39–1.44 (m, 2H, CH_2), 1.77–1.79 (m, 1H, CH), 2.14–2.19 (m, 1H, CH), 3.15–3.16 (d, J = 4 Hz, 1H, CH), 7.47–7.53 (m, 4H, aromatics CH), 7.76–7.78 (d, J = 8 Hz, 1H, aromatics CH), 7.86–7.90 (t, 2H, aromatics CH). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3): δ = 10.81, 19.69, 20.67, 27.64, 34.04, 48.53, 53.07, 62.90, 124.13, 124.79, 124.96, 126.48, 126.84, 127.28, 127.80, 128.98, 131.09, 134.08, 136.97, 139.94, 156.89. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a THF solution of the compound (50.0 mg in 5.0 mL) at room temperature.

2.3. X-Ray Structure Determination of 3,3'-Bi(1,1'-dinaphthyl-camphopyrazole) 1. X-ray diffraction data were collected using an Agilent, Eos, Gemini diffractometer with enhanced X-ray source (Mo- $\text{K}\alpha$ radiation, λ = 0.71073 Å). Data collection, cell refinement, data reduction, structure solving, and refining were performed by using the following programs: CrysAlis PRO [10]; CrysAlis PRO [10]; CrysAlis RED [10]; ShelXT [11]; SHELXL [12]. Molecular graphics: Olex2 [13] was used to prepare the material for publication. Crystal data and experimental details are listed in Table 1. All H atoms were located in difference maps. The C–H atoms were treated as riding atoms in geometrically idealized positions with C–H distances of 0.95 Å (CH) and 0.99 Å (CH_2) and refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The CH_3 atoms were treated as riding atoms in geometrically idealized positions with the CH_3 distances of 0.98 Å and refined with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$. The Platon SQUEEZE program [14] was used to get rid of the solvent peaks. Absolute configurations were determined using 2351 quotients $[(I+) - (I-)] / [(I+) + (I-)]$ [15]. Supplementary crystallographic data for **1** are contained in CCDC 1458095. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: 144-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk/>), or from the authors.

TABLE 1: Crystal data and experimental crystallographic details.

	Compound 1
Empirical formula	$\text{C}_{42}\text{H}_{42}\text{N}_4$
Formula weight	602.79
Temperature	173 K
Crystal system, space group	Monoclinic, $P2_1$
Unit cell dimensions	$a = 7.4986(4)$ Å $b = 25.7037(16)$ Å $c = 10.7306(5)$ Å $\beta = 104.001(5)^\circ$
Volume	$2006.78(19)$ Å ³
Z, calculated density	2, 0.998 Mg m^{-3}
Absorption coefficient	0.06 mm^{-1}
$F(000)$	644
Crystal size	$0.42 \times 0.28 \times 0.22$ (mm)
θ range for data collection	3.8 to 32.0°
Index ranges	$-10 \leq h \leq 10$, $-32 \leq k \leq 38$, $-15 \leq l \leq 16$
Reflections collected	15094
Independent reflections	10751 [$R_{\text{int}} = 0.041$]
Data/restraints/parameters	10751/1/421
Goodness-of-fit on F^2	1.03
Final R indices [$I > 2(I)$] ^a	$R_1 = 0.077$, $wR_2 = 0.1823$
R indices (all data)	$R_1 = 0.1011$, $wR_2 = 0.2005$
Largest diff. peak and hole	0.30 and -0.37 e Å^{-3}
Absolute structure parameter	$-1.6(10)$

^a $w = 1/[\sigma^2(F_o^2) + (0.0881P)^2 + 0.4493P]$, where $P = (F_o^2 + 2F_c^2)/3$.

3. Results and Discussion

3,3'-Bi(1,1'-dinaphthyl-camphopyrazole) **1** was prepared by condensation reaction between bis-1,3-diketone and α -naphthylhydrazine hydrochloride (Scheme 1). The identity

FIGURE 1: View of 3,3'-bi(1,1'-dinaphthyl-camphopyrazole) **1** showing the atom-labelling. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°) are N1–N2 1.377(4), N2–C1 1.354(4), C1–C2 1.446(4), C2–N4 1.346(4), N4–N3 1.365(4), N1–N2–C1 104.9(2), N2–C1–C2 119.7(3), C1–C2–N4 119.6(3), and C2–N4–N3 105.6(3).

of the compound was established by ^1H and ^{13}C NMR spectroscopy and elemental analysis. Crystals suitable for an X-ray crystal structure determination grew from slow evaporation of a tetrahydrofuran solution of the compound at room temperature. It consists of a 3,3'-bipyrazole group with *E* configuration. Each pyrazole ring contains a fused camphor group and a naphthalene ring bonded to the adjacent nitrogen atom in the ring (Figure 1). The bond lengths and angles values found for the fused camphor group correspond with characteristic values reported in similar compounds [16].

1 crystallizes in the space group $P2_1$ with two independent molecules in the unit cell. The dihedral angle between the mean planes of the two pyrazole rings is $3.9(1)^\circ$. The mean planes of the naphthalene rings are tilted by $88.8(1)^\circ$ and $88.8(2)^\circ$ with regard to that of the pyrazole ring and $2.1(3)^\circ$ with each other. The mean plane of the 5-membered ring of the camphor group is twisted by $44.2(3)^\circ$ and $44.2(1)^\circ$, respectively, with that of the pyrazole ring forming an indazole-like altered motif. Both of the trimethyl, 5-membered rings of the fused camphor group form an envelope with the apex carbon (C19, $\varphi = 252.5(4)$ and C39, $\varphi = 252.9(4)$) forming the flap atom in each case. In the crystal, weak π – π stacking interactions are observed between nearby 6-carbon rings (Cg1 and Cg2) of the two naphthalene rings (Cg1–Cg2 = $3.644 \text{ \AA}$; $1+x, +y, 1+z$; where Cg1 = C11/C12/C7/C8/C9/C10 and Cg2 = C31/C32/C27/C28/C29/C30) linking the molecules into extended chains (Figure 2).

TABLE 2: Distances and angles (Å, °) of hydrogen bonding interactions. The H atoms are in calculated positions (D: donor; A: acceptor; H: hydrogen).

D–H...A	H...A	D...A	D–H...A
C4–H4...Cg4	2.91	3.698(4)	141
C24–H24...Cg3	2.93	3.747(4)	144

Cg3 = N1/N2/C1/C13/C18; Cg4 = N3/N4/C2/C33/C38; symmetry codes: (i) $x+1, y, z$; (ii) $x-1, y, z$.

Weak π –ring intermolecular interactions are also seen between naphthalene atoms and pyrazole rings from each of the groups helping to stabilize the crystal packing. No classical hydrogen interactions ($\text{C–H}\cdots\pi$) are formed (Table 2).

4. Summary

The compound 3,3'-bi(1,1'-dinaphthyl-camphopyrazole) **1** has been prepared and characterized by NMR spectroscopy, elemental analysis, and single crystal X-ray diffraction. The solid-state structure shows the spatial arrangement of the naphthyl groups with respect to the pyrazole ring and intermolecular interactions that sustain the crystal.

Competing Interests

The authors declare that they have no competing interests.

FIGURE 2: Molecular packing of 3,3'-bi(1,1'-dinaphthyl-camphopyrazole) **1** viewed along the *a* axis.

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