Synthesis, characterization and crystal structures of two 2-naphthyl substituted pyrazoles

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The synthesis, characterization and X-ray crystal structures of two 2-naphthyl-substituted pyrazoles - 3-(2-naphthyl) pyrazole (**1**) and 5-(2-naphthyl)-3-trifluoromethyl-pyrazole (**3**) - are reported. In addition, the isolation and structural characterization of 5-hydroxy-3-(2-naphthyl)-5-trifluoromethyl-4,5-dihydropyrazole (**2**), an intermediate of the synthesis of **3**, is included. Two simple methods of dehydration of **2** are also presented.

Pyrazoles without substitution at their nitrogen 1-position (1H-pyrazoles) crystallize in either one of two groups comprising four distinct classes of N1-H⋯N2 hydrogen-bonded units – dimers and tetramers in the first group, trimers and catemers (chains) in the second. Foces-Foces *et al.* have devised a simple empirical rule based on the sum of molecular refractivity values of the substituents at the pyrazole positions-3 and -5 ($MR_{3,5}$), that predicts correctly to which one of the two above groups belongs each one of more than fifty pyrazoles and related compounds [1]. According to that rule, a pyrazole with $MR_{3,5}$ < 2.4 is expected to exist as a trimer or catemer in its crystalline form. In contrast, pyrazoles with $MR_{3,5}$ > 2.4 prefer dimeric or tetrameric associations. However, a few exceptions to the rule do exist [2,3]. In order to evaluate the breadth of applicability of this rule and illuminate the reasons of its occasional failure, pyrazoles with a variety of substituent types need to be structurally studied. Interestingly, some analogous structures are known for pyrazolato complexes of linear two-coordinate d^{10} metals. Binary group-11 metal pyrazolato trimers, tetramers and catemers - structural analogues of pyrazoles with metals in the place of bridging hydrogen atoms - have been characterized [4]. However, the parallel between pyrazoles and metal pyrazolates is only partial; pyrazole dimers do not have a binary metal pyrazolate analogue, neither does the hexameric gold(I)-3,5-diphenylpyrazolate have a corresponding pyrazole structure [5]. As part of our search of further structural variations in metal pyrazolates we have embarked on an effort to prepare 3(5)- and 3,5-substituted

Scheme 1
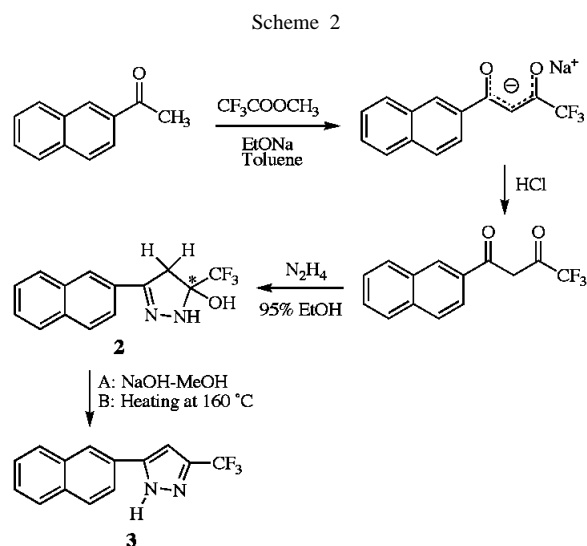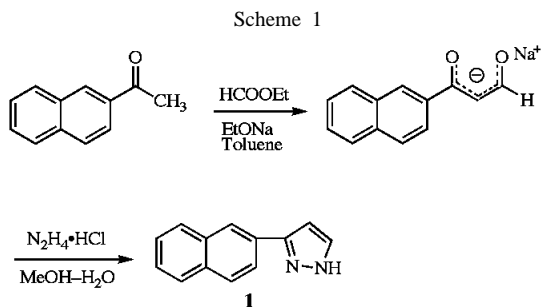
pyrazoles with sterically demanding substituents and study their solid state structures along with those of their binary metal complexes.

Compounds containing the bulky 2-naphthyl group are often involved in supramolecular architectures *via* - interactions. The high MR value, 4.16 [6], of this group alone indicates that pyrazoles containing it at their 3- or 5-position should form dimers or tetramers, according to Foces-Foces' empirical rule [1]. In this paper, we report the synthesis, characterization and X-ray crystal structures of two 2-naphthyl-substituted pyrazoles, 3-(2-naphthyl) pyrazole (**1**) and 5-(2-naphthyl)-3-trifluoromethyl-pyrazole (**3**). In addition, the isolation and structural characterization of 5-hydroxy-3-(2-naphthyl)-5-trifluoromethyl-4,5-dihydropyrazole (**2**), an intermediate of the synthesis of **3**, is included. Two simple methods of dehydration of **2** are also presented.

Results and Discussion.

Synthesis.

3-(2-Naphthyl)pyrazole (**1**) was prepared by a modification of the procedure reported by S. Trofimenko *et al.* (Scheme 1) [7]. The reaction of hydrazines with -dicar-
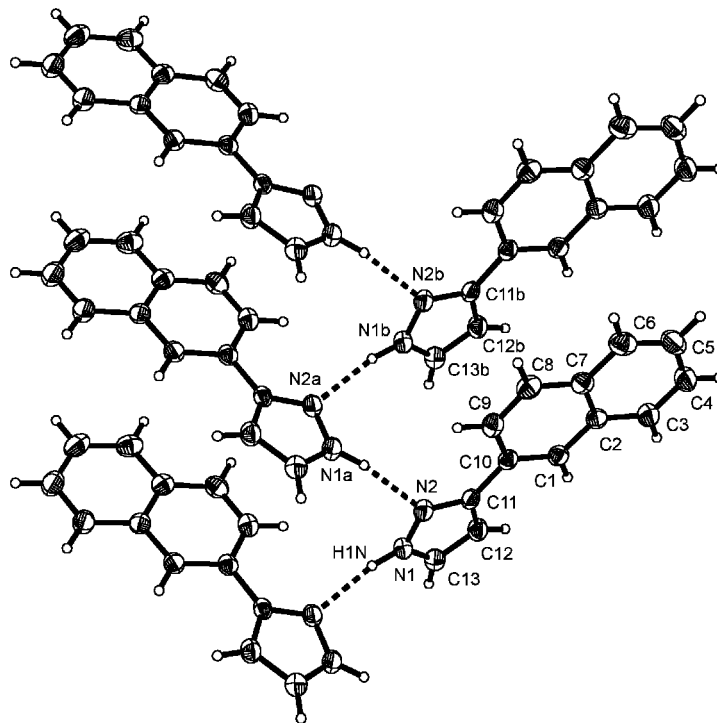
Scheme 2

Figure 1. ORTEP diagram of the helix of **1** showing the H-bonding pattern. Symmetry codes: (a) *x*+1/2, -*y*+3/2, -*z*+2; (b) x-1, y, z.

Table 1

Crystal Data and Structure Refinements for **1**, **2** and **3**

|	**1**	**2**	**3**
Empirical formula	$C_{13}H_{10}N_2$	$C_{14}H_{11}F_3N_2O$	$C_{14}H_9F_3N_2$
Formula weight	194.23	280.25	262.23
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\,2_12_12_1$ (No. 19)	$P\,2_1$ (No. 4)	$P\,2_1/n$ (No. 14)
a, Å	5.236(1)	9.050(2)	9.513(2)
b, Å	10.733(2)	5.578(1)	5.725(1)
c, Å	17.638(3)	12.801(2)	23.000(5)
, deg	90	90	90
, deg	90	105.279(4)	101.936(3)
, deg	90	90	90
Volume, Å^3	991.2(3)	623.3(2)	1225.5(5)
Z	4	2	4
Density (calc.), Mg m^{-3}	1.302	1.493	1.421
Absorption coefficient, mm^{-1}	0.079	0.126	0.118
range for data collection, deg	2.22 to 23.30	1.65 to 28.69	1.81 to 28.69
Reflections collected	4347	4561	5441
Independent reflections	1426 [*R*(int) = 0.0387]	2572 [*R*(int) = 0.0549]	2742 [*R*(int) = 0.0657]
Data/restraints/parameters	1426 / 0 / 141	2572 / 1 / 197	2742 / 0 / 204
Goodness-of-fit on F^2	1.034	0.915	1.056
Final *R* indices [*I* > 2 (*I*)]	*R*1 = 0.0284,	*R*1 = 0.0493,	*R*1 = 0.0708,
	*wR*2 = 0.0745	*wR*2 = 0.0995	*wR*2 = 0.2005
R indices (all data)	*R*1 = 0.0314,	*R*1 = 0.1258,	*R*1 = 0.0997,
	*wR*2 = 0.0765	*wR*2 = 0.1389	*wR*2 = 0.2259
Largest diff. peak and hole, e Å^{-3}	0.099 and -0.093	0.215 and –0.213	0.205 and – 0.214
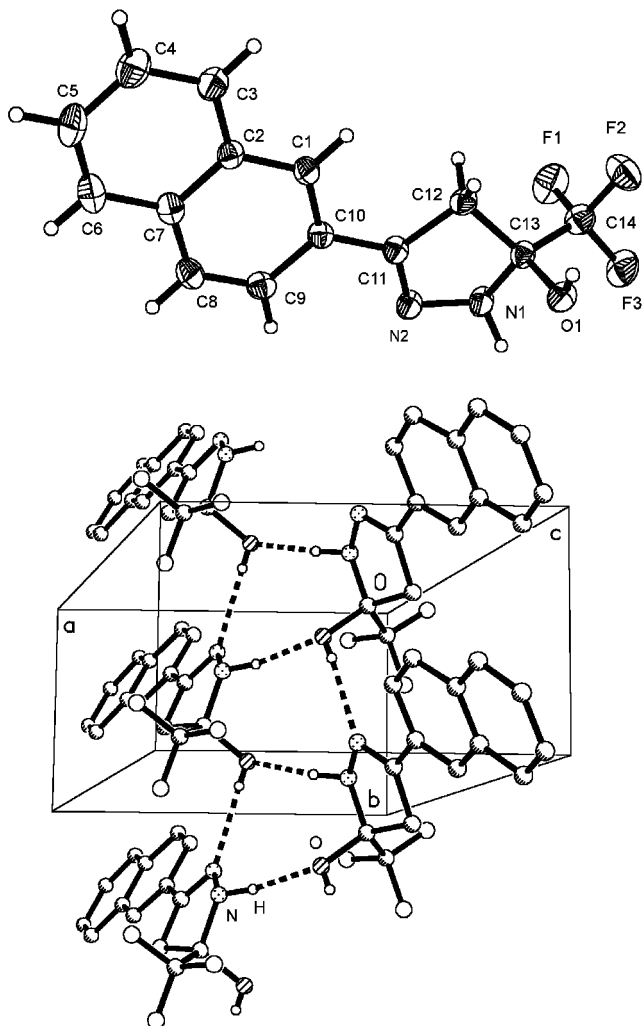
Figure 2. a) ORTEP diagram of **2** with the atomic labeling scheme. b) Ball-and-stick diagram of **2** showing intermolecular H-bonds.

bonyls is a common pyrazole synthesis. 5-Hydroxy-4,5-dihydropyrazoles have been detected by nmr during such reactions and are regarded as key intermediate species [8]. Intermediates of this type are not stable, as they can be readily dehydrated to the corresponding pyrazoles, and are typically not isolated. However, the presence of a strong electron-withdrawing substituent, such as $-CF_3$, on the -diketone can stabilize 5-hydroxy-4,5-dihydropyrazoles and allow their isolation. Subsequent dehydration by reflux in acidified solvents leads to a pyrazole [9,10]. The reaction of hydrazine with 1-trifluoromethyl-3-(2-naphthyl)-propanedione in toluene yielded compound **2**, which is characterized by solution nmr and single crystal X-ray crystallography (Scheme 2). However, refluxing **2** in toluene failed to give the expected dehydration product. Instead, the desired pyrazole, **3**, was prepared efficiently by dehydration of **2** carried out either by treatment with NaOH in MeOH, or by heating a solid sample of **2** at a temperature >160 °C. The progress of the latter reaction can be monitored by differential thermal analysis (DTA) and thermogravimetric (TG) techniques. Three endothermal peaks at 136.5, 162.7 and 177.8 °C are evident in the DTA curve of a fresh sample of **2**. When the same sample was scanned for a second run, only one peak at 179.5 °C, associated with the melting point, was observed. Consequently, the endothermal peaks at 136.5 and 162.7 °C are attributed to the dehydration process, which produces **3**. TG analysis shows that the sample of **2** begins to loose weight at *ca.* 140 °C, in accord with the DTA result. Between 140 and *ca.* 265 °C compound **3** sublimes, as evident by a gradual, further weight loss, until the sample vanishes.

X-Ray Structures.

The X-ray crystal structures of compounds **1** - **3** (Figures 1-3) are in agreement with the solution spectroscopic data. Crystallographic parameters pertaining to the
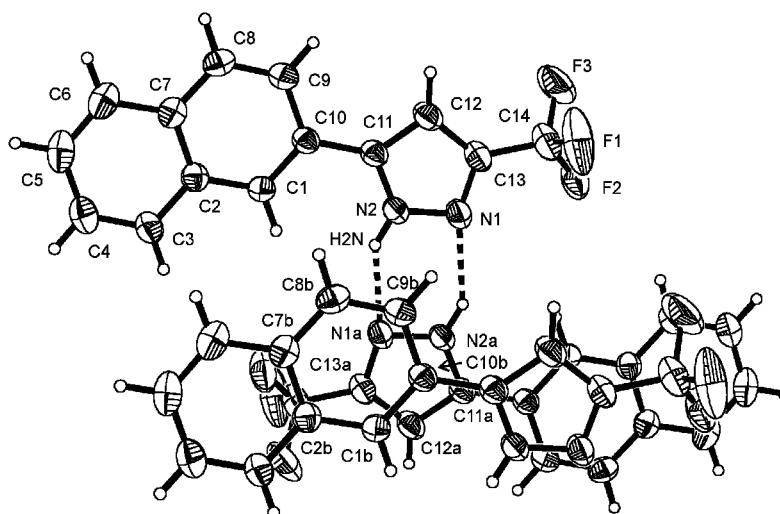

Figure 3. ORTEP diagram of **3** showing the H-bonding pattern and the off-set - stacking. Symmetry code: a) -x+1, -y, -z; b) x, y-1, z.

Table 2

Fractional Atomic Coordinates [x10^4] and Equivalent Isotropic
Displacement Parameters ($Å^2$) for **1**, **2** and **3**

1

Atom	x	y	z	U(eq)
C1	8870(4)	5908(1)	7441(1)	48(1)
C2	7054(3)	6168(1)	6870(1)	47(1)
C3	6920(4)	5468(2)	6192(1)	60(1)
C4	5167(4)	5743(2)	5650(1)	68(1)
C5	3440(4)	6731(2)	5754(1)	71(1)
C6	3505(4)	7425(2)	6400(1)	66(1)
C7	5334(3)	7164(1)	6979(1)	50(1)
C8	5513(4)	7871(2)	7653(1)	56(1)
C9	7306(3)	7612(2)	8188(1)	52(1)
C10	9026(3)	6603(1)	8094(1)	44(1)
C11	10979(3)	6312(1)	8669(1)	43(1)
C12	12645(3)	5301(2)	8696(1)	53(1)
C13	14175(4)	5494(2)	9310(1)	55(1)
N1	13415(3)	6557(1)	9630(1)	54(1)
N2	11445(3)	7090(1)	9250(1)	50(1)
H1N	14210	6974	10026	78

2

Atom	x	y	z	U(eq)
C1	7882(5)	5198(7)	1280(3)	40(1)
C2	7895(4)	4540(8)	208(3)	36(1)
C3	8640(5)	5941(8)	-412(3)	48(1)
C4	8597(6)	5292(10)	-1455(4)	61(1)
C5	7825(6)	3241(10)	-1902(4)	61(2)
C6	7106(5)	1833(9)	-1322(3)	57(1)
C7	7118(4)	2435(8)	-243(3)	44(1)
C8	6355(5)	1072(8)	383(3)	46(1)
C9	6335(5)	1772(7)	1385(3)	43(1)
C10	7120(5)	3874(7)	1864(3)	36(1)
C11	7057(5)	4680(7)	2947(3)	38(1)
C12	7783(6)	6943(8)	3498(3)	40(1)
C13	6990(5)	7148(7)	4408(3)	39(1)
C14	7988(6)	8006(9)	5484(4)	53(1)
F1	9255(3)	6676(6)	5833(2)	83(1)
F2	8452(3)	10275(5)	5433(2)	75(1)
F3	7236(3)	7937(6)	6254(2)	73(1)
N1	6543(5)	4723(6)	4527(3)	48(1)
N2	6362(4)	3485(6)	3541(3)	45(1)
O1	5682(4)	8662(6)	4141(2)	46(1)
H12A	7590	8350	3040	18
H12B	8870	6740	3740	57
H1N	5730	4510	4830	120
H1O	5810	9710	3880	24

3

Atom	x	y	z	U(eq)
C1	5535(2)	4486(4)	1320(1)	59(1)
C2	5280(2)	5723(4)	1818(1)	58(1)
C3	4317(3)	4900(5)	2164(1)	72(1)
C4	4101(3)	6121(6)	2645(1)	84(1)
C5	4833(3)	8209(7)	2802(1)	91(1)
C6	5766(3)	9070(5)	2480(1)	80(1)
C7	6022(2)	7851(4)	1977(1)	61(1)
C8	6996(2)	8633(4)	1631(1)	67(1)
C9	7222(2)	7391(4)	1155(1)	62(1)
C10	6486(2)	5276(4)	987(1)	55(1)
C11	6752(2)	3957(4)	476(1)	56(1)
C12	7753(3)	4175(5)	123(1)	74(1)
C13	7475(2)	2362(5)	-281(1)	66(1)
C14	8236(3)	1723(7)	-763(1)	88(1)
F1	9391(7)	585(19)	-595(2)	168(3)
F2	7414(4)	605(11)	-1197(2)	110(2)

Table 2 (continued)

F3	8635(9)	3641(10)	-1023(3)	159(3)
F4	8320(20)	-777(19)	-814(10)	141(5)
F5	7850(30)	2450(70)	-1244(6)	204(12)
F6	9578(14)	1950(40)	-559(9)	143(9)
N1	6375(2)	1067(4)	-205(1)	69(1)
N2	5959(2)	2106(4)	257(1)	65(1)
H2N	5220	1470	370	87

Table 3

Bond Lengths (Å) and Bond Angles (deg) for **1**, **2** and **3**

1

C11-N2	1.345(2)	C13-N1	1.333(2)
C11-C12	1.393(2)	N1-N2	1.357(2)
C12-C13	1.364(2)		
N2-C11-C12	110.1(1)	C13-N1-N2	112.3(1)
C13-C12-C11	106.1(1)	C11-N2-N1	104.6(1)
N1-C13-C12	106.9(2)		

2

C11-N2	1.292(4)	C13-C14	1.512(6)
C11-C12	1.510(6)	C14-F3	1.338(5)
C12-C13	1.525(5)	C14-F1	1.340(5)
C13-O1	1.420(5)	C14-F2	1.340(6)
C13-N1	1.431(5)	N1-N2	1.409(5)
N2-C11-C10	122.8(3)	F3-C14-F1	107.2(4)
N2-C11-C12	112.1(3)	F3-C14-F2	106.8(4)
C11-C12-C13	100.7(3)	F1-C14-F2	106.7(4)
O1-C13-N1	110.2(3)	F3-C14-C13	111.4(4)
O1-C13-C14	106.9(3)	F1-C14-C13	112.5(4)
N1-C13-C14	108.7(3)	F2-C14-C13	112.0(4)
O1-C13-C12	113.0(3)	N2-N1-C13	109.7(3)
N1-C13-C12	102.3(3)	C11-N2-N1	108.3(3)
C14-C13-C12	115.6(4)	F3-C14-F1	107.2(4)

3

C11-N2	1.337(3)	C13-N1	1.323(3)
C11-C12	1.379(3)	N1-N2	1.347(3)
C12-C13	1.381(4)	C13-C14	1.489(4)
N2-C11-C12	104.7(2)	C13-N1-N2	103.1(2)
C11-C12-C13	105.6(2)	C11-N2-N1	114.3(2)
N1-C13-C12	112.3(2)		

structure determinations of **1** – **3** are summarized in Table 1, while the corresponding atomic coordinates and equivalent isotropic displacement parameters are listed in Table 2. Selected bond distances and bond angles for compounds **1** - **3** are listed in Table 3. In both pyrazole structures, the naphthyl and pyrazole rings are nearly coplanar, with small dihedral angles of 10.1(1) and 9.4(2)° between them, for **1** and **3**, respectively. The hydrogens of the pyrazole N-H have been located from difference Fourier maps. Thus, the preferred tautomers, 3-(2-naphthyl) for **1** and 5-(2-naphthyl) for **3**, are identified unequivocally and are consistent with the Hammet parameter order, CF_3- > 2-naphthyl- >H-, of the substituents occupying the 3- and 5-position of the pyrazole

Table 4

Parameters of the Potential C-H··· Interactions for **1**, **2** and **3**.

C-H···A [a] (symmetry)	C-H (Å)	H···A (Å)	C-H···A (deg)
1			
C12-H12···C8 (-x+2, y-1/2, -z+3/2)	0.93	2.764	161.63
C12-H12···C7 (-x+2, y-1/2, -z+3/2)	0.93	2.902	148.01
C3-H3···N2 (-x+2, y-1/2, -z+3/2)	0.93	3.001	145.64
C4-H4···C13 (-x+1, y+3/2, -z-1/2)	0.93	2.866	130.17
C4-H4···N4 (-x+1, y+3/2, -z-1/2)	0.93	2.882	133.35
C8-H8···C3 (-x+1, y+1/2, -z+3/2)	0.93	2.899	142.33
C8-H8···C2 (-x+1, y+1/2, -z+3/2)	0.93	3.016	158.18
2			
C3-H3···C2 (-x+2, y+1/2, -z)	0.93	2.966	134.06
C3-H3···C3 (-x+2, y+1/2, -z)	0.93	2.790	162.10
C3-H3···C4 (-x+2, y+1/2, -z)	0.93	2.958	157.85
C8-H8···C8 (-x+1, y-1/2, -z)	0.93	2.784	160.05
C8-H8···C9 (-x+1, y-1/2, -z)	0.93	2.856	156.50
C8-H8···C7 (-x+1, y-1/2, -z)	0.93	3.015	132.26
3			
C6-H6···C7 (-x+3/2, y+1/2, -z+1/2)	0.93	2.925	147.36
C6-H6···C8 (-x+3/2, y+1/2, -z+1/2)	0.93	2.837	156.05

[a] Atoms in the aromatic rings involved.

rings [1]. 3-(2-Naphthyl)pyrazole, **1**, crystallizes in the chiral space group P2$_1$2$_1$2$_1$. The order-2 helix of **1**, running parallel to the *a*-axis in its crystal, is held together by weak N-H···N hydrogen-bonds (N1···N2a = 2.921(2) Å) and - stacking [11,12] between naphthyl groups (C1-C10) and the pyrazoles (C11b – C13b, N1b, N2b) in an offset manner (plane-plane distance, *ca.* 3.31 Å; centroid-centroid distance, 3.78 Å; dihedral angle, 10.1°) (Figure 1). Between neighboring helical catemers, edge-to-face - interactions (C-H···) [13] exist in the crystal of **1**, as judged by the H···C distances and angles at the H atoms involved (Table 4). On the other hand, the dimeric structure of **3** is supported by a symmetric pair of slightly stronger H-bonds between two pyrazole groups (N1···N2a = 2.852(3) Å), besides the presence of the strongly electron withdrawing -CF$_3$ group close to the nitrogen lone electron pair. The offset - stacking between neighboring naphthyl and pyrazole rings, such as the planes (C1b, C2b, C7b – C10b) and (N1a, N2a, C11a – C13a) shown in Figure 3, are observed in **3** with a plane-plane distance of *ca.* 3.67 Å, centroid-centroid distance of 4.17 Å, and dihedral angle of 9.4°. Here again, the potential edge-to-face - interactions (C-H···) are found in the crystal of **3** (Table 4). While the dimeric structure of **3** with a MR$_{3,5}$ value of 4.66 (= 4.16 + 0.50), conforms to the empirical rule ofFoces-Foces, that of **1** with MR$_{3,5}$ = 4.26 (= 4.16 + 0.10) does not. MR is usually employed as a steric parameter for organic substituents. Therefore, prediction of the H-bonding patterns of pyrazole by using MR$_{3,5}$ only reflects the repulsions between these substituents. The presence of bulky naphthyl groups in

compounds **1** and **3** facilitates the - interactions between naphthyl groups and/or pyrazole rings. Thus, the final H-bonding patterns of **1** and **3** is dictated not only by repulsions between substituents and H-bonds between pyrazoles, but also the - interactions between naphthyl groups and/or pyrazole rings.

Compound **2** contains a chiral center and crystallizes in the chiral P2$_1$ space group. H-bonds involving nitrogen atoms and OH- groups contribute to the formation of double helical chains (order-2) along the *b*-axis as illustrated in Figure 2 (N1-H···O1a = 3.020(5) Å, O1-H···N2b = 2.907(5) Å; symmetry codes: a) –x+1, y-1/2, -z+1; b) x, y+1, z).

EXPERIMENTAL

Physical Measurements.

Melting points were measured on an Electrothermal IA9100 digital melting point apparatus. Elemental analyses were performed by Galbraith Laboratories, Inc. (Knoxville, TN). [1]H-nmr and ^{13}C-nmr spectra were recorded on a Bruker Advanced DRX-500 spectrometer. FT-IR spectra were recorded on KBr pellets in the range 4000 - 400 cm^{-1} with a Nicolet Magna-IR 750 spectrometer. Mass spectra were measured on a Micromass Autospec High Resolution Mass Spectrometer. DSC curves were obtained by a Perkin Elmer DSC 6 Differential Scanning Calorimeter. TG data were obtained on a Shimadzu TGA 50 analyzer in air at a heating rate of 10 °C minute[-1].

3-(2-Naphthyl)pyrazole (**1**).

To a rapidly stirred slurry of anhydrous sodium ethoxide (3.4 g, 0.05 mol) in 100 mL of dry toluene, was added a 2'-aceto-naphthone (8.5 g, 0.05 mol)-ethyl formate (5.6 g, 0.075 mol) mixture and a gelatinous material formed rapidly. After stirring for 12 hours, the resulting ketaldehyde (yellow powder) was collected by filtration and washed with toluene and hexane. To a slurry of the yellow solid in 50 mL MeOH, a solution of hydrazine monohydrochloride (3.4 g, 0.05 mol) in 50 mL H$_2$O was added with stirring. After 1 hour, the resulting mixture was extracted with CH$_2$Cl$_2$ (3 x 80 mL). After removing the solvent from the extract on a rotary evaporator, **1** was obtained as a pale yellow solid, which, after recrystallization from warm toluene, yielded 8.1 g (83%) of pale yellow needles, mp 158-159 °C; ir (KBr pellet): 3142 (NH), 3050, 2906, 1540 (C=N), 1470, 1370, 1185, 1047, 972, 928, 895, 863, 820, 778, 760, 607, 475 cm^{-1}; ^{1}H nmr (DMSO-d$_6$): 12.91 (br, s, 1H, NH), 8.25 (d, 1H, *J* = 2.0 Hz, pyrazole 5-H), 7.98 (d, 1H, *J* = 8.5 Hz, naphthyl), 7.87 (d, 2H, *J* = 8.3 Hz, naphthyl), 7.83 (d, 1H, *J* = 7.9 Hz, naphthyl), 7.63 (s, 1H, naphthyl), 7.46 (m, 2H, naphthyl), 6.73 ppm (d, 1H, *J* = 2.0 Hz, pyrazole 4-H); ^{13}C nmr (DMSO-d$_6$): 133.0, 132.2, 127.7, 127.5, 127.2, 125.8, 125.3, 123.6, 123.1, 101.7 ppm (pyrazole 4-C) ppm; EI ms: m/z 195.0894 M$^+$+1 (17.4), 194.0837 M$^+$ (100), 166.0850 M$^+$-N$_2$ (13.3), 165.0848 (37.8).

3-(2-Naphthyl)-5-hydroxy-5-trifluoromethyl-4,5-dihydropyrazole (**2**).

To a rapidly stirred slurry of anhydrous sodium ethoxide (3.4 g, 0.05 mol) in 60 mL of dry toluene, was added in one portion a

mixture of 2'-acetonaphthone (8.5 g, 0.05 mol) and methyl trifluoroacetate (8.87 g, 0.05 mol). The mixture was stirred for 12 hours, then it was neutralized by aqueous HCl. After toluene had been removed by evaporation, the residue was recrystallized from aqueous ethanol to yield 2-naphthoyltrifluoroacetone [14]. The -diketone was taken up in 50 mL of warm 95% ethanol. To the solution, hydrazine monohydrate (2.5 g, 0.05 mmol) was added dropwise. After cooling down, white powder was obtained, 7.0 g (50%), ir (KBr pellet): 3312 (OH), 3158 (NH), 3050, 2916, 1600,1449, 1351, 1334, 1255 (CF_3), 1199, 1185, 1170, 1133, 1065, 1032, 958, 904, 864, 856, 833, 753, 710, 509, 481 cm^{-1}; ^1H nmr (DMSO-d_6):   8.03 (d, 1H, J = 9.4 Hz, naphthyl), 7.93 (m, 3H, naphthyl), 7.51 (m, 2H, naphthyl), 7.36 (s, 1H, naphthyl), 3.48 (d, 1H, J = 16.8 Hz, pyrazole 4-H), 3.35 ppm (d, 1H, J = 16.8 Hz, pyrazole 4-H); ^{13}C nmr (DMSO-d_6):   147.5 (pyrazole 3-C), 132.9, 132.8, 129.8, 128.1, 128.0, 127.6, 126.6, 126.5, 125.4, 124.2 (q, $^1J_{C\text{-}F}$ = 282.6 Hz, CF_3), 122.8, 91.1 (q, $^2J_{C\text{-}F}$ = 30.4 Hz, pyrazole 5-C), 41.3 ppm (pyrazole 4-C); EI ms: m/z 280.0802 M$^+$ (11.5), 263.0777 M$^+$-OH (14.3), 262.0631 M$^+$-H_2O (100).

Anal. Calcd. for $C_{14}H_{11}N_2OF_3$: C, 59.95; H, 3.93; N, 9.99. Found: C, 60.04; H, 3.93; N, 9.96. Single crystals of X-ray quality are grown by slow evaporation of a diethylether solution of **2**.

3-Trifluoromethyl-5-(2-naphthyl)-pyrazole (**3**).

Method A.

3-(2-Naphthyl)-5-hydroxy-5-trifluoromethyl-4,5-dihydropyrazole (**2**) (1.0 g, 3.5 mmol) and NaOH (0.28 g, 7 mmol) were mixed in methanol with stirring. The two solids gradually dissolved and the solution became clear. After one day, the solvent evaporated to dryness and the residue was extracted with hot toluene. After cooling, large colorless crystals precipitated from the toluene solution in 0.57 g (60%) yield.

Method B.

In a test tube, neat 3-(2-naphthyl)-5-hydroxy-5-trifluoromethyl-4,5-dihydropyrazole (**2**) was heated to 160 °C in an oil bath for 30 minutes. After the molten product had cooled down and solidified, it was recrystallized from toluene giving colorless prismatic crystals in 70% yield, mp 178 –179 °C; ir (KBr pellet): 3235 (NH), 3060, 1606, 1581, 1567, 1501, 1418, 1297, 1258 (CF_3), 1156, 1123, 1109, 1057, 994, 977, 890, 862, 826, 807, 743, 716, 682, 477 cm^{-1}; ^1H nmr (DMSO-d_6):   8.41 (s, 1H, pyrazole 4-H), 8.04 – 7.93 (m, 4H, naphthyl), 7.56 (m, 2H, naphthyl), 7.33 (s, 1H, naphthyl); ^{13}C nmr (DMSO-d_6):   144.0 (pyrazole 5-C), 142.1 (q, $^2J_{C\text{-}F}$ = 36.9 Hz, pyrazole 3-C), 132.9, 132.8, 128.8,128.1, 128.1, 127.7,126.9, 126.8, 125.4, 124.4, 123.4, 121.8 (q, $^1J_{C\text{-}F}$ = 268.2 Hz, CF_3), 101.4 ppm (pyrazole 4-C); EI ms: m/z 263.0742 M$^+$+1 (19.1), 262.0701 M$^+$ (100), 165.0665 M$^+$-(H+N_2+CF_3) (17.1).

Anal. Calcd. for $C_{14}H_9N_2F_3$: C, 64.07; H, 3.43; N, 10.68. Found: C, 64.08; H, 3.47; N, 10.70.

X-ray Crystallography.

Single crystals were mounted atop glass fibers with epoxy glue. Diffraction measurements were carried out with a Siemens SMART 1K CCD diffractometer with graphite monochromated Mo-K   (λ = 0.71073 Å) radiation. Data

corrected for Lorentz and polarization effects were employed for crystal structure determination by direct method and structure refinement based on F^2 using the SHELXTL crystallographic package programs [15]. All non-hydrogen atoms were refined anisotropically, while H-atom positions were not refined. All the H-atom positions on aromatic rings were calculated at ideal positions, while other H-atoms including N-H, O-H and CH_2 were located from the difference fourier maps. For **3**, due to the disorder of CF_3 groups, six F-atoms are used to model this group with occupancy factors fixed at 0.75 (F1 – F3) and 0.25 (F4 – F6). Other important crystallographic and experimental data are listed in Table 1.

Supplementary Material.

X-ray crystallographic files (CIF) have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 205587 - 205589 for compound **1**, **2** and **3**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

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