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Preparation and structures of some new 1*H*-pyrazole derivatives

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Abstract Some new 3,5-diaryl-1*H*-pyrazoles were prepared from aryl methyl ketones via Claisen condensation with aromatic esters and followed by cyclization with hydrazine monohydrate. Their structures were confirmed by IR, ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. The X-ray structure for 3(5)-(4-*tert*-butylphenyl)-5(3)-(4-methoxyphenyl)-1*H*-pyrazole (**2b**) was presented. The results show that compound **2b** exists as tautomers **I** and **II**, and its molecules are connected by the N–H···N intermolecular hydrogen bonds to form cyclic dimers consisting of the tautomers **I** and **II**.

Keywords 1*H*-Pyrazole · Preparation · Crystal structure · Hydrogen bonds

Introduction

Pyrazoles are of great interest to the biochemical community due to their wide range of biological activities, such as analgesic, antimicrobial, anti-inflammatory and antihypertensive properties [1–3]. Recently, we have synthesized some aromatic 1,3-diketones used as ultraviolet absorbents [4]. As 1,3-diketones are well-known intermediates in the broadest and most efficient route to 1*H*-pyrazoles [5–7], we undertook studies on 1*H*-pyrazole derivatives as an extension of our previous work. Currently, we have studied the structures and anti-microbial activity of some substituted pyrazoles [8, 9]. In this paper, some new 1*H*-pyrazoles were prepared and characterized by FTIR, ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. The compound 3(5)-(4-*tert*-butylphenyl)-5(3)-(4-methoxyphenyl)-1*H*-pyrazole (**2b**) was used to carry out the X-ray structure determination.

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Experimental

Materials and methods

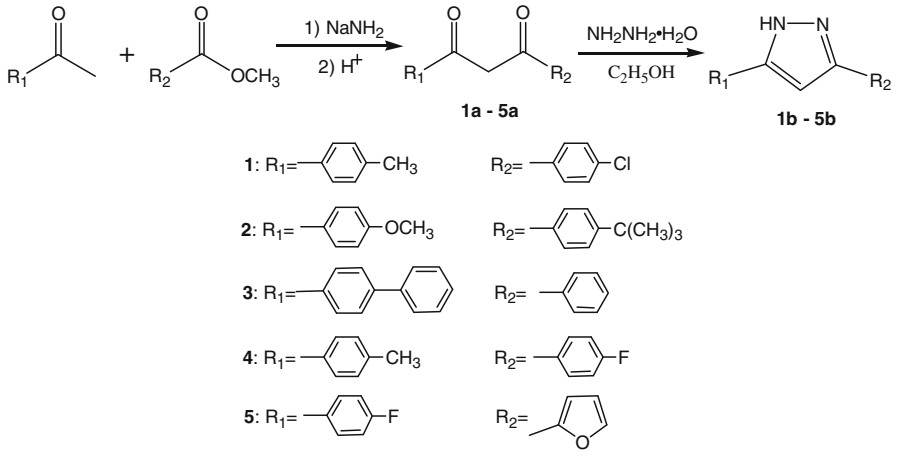
All reagents and solvents were purchased from commercial sources, and were used without further purification. Melting points were determined by X-4 digital melting-point apparatus and are uncorrected. Elemental analysis (C, H, N) was performed using a Perkin-Elmer 2400 elemental analyzer. ^{1}H NMR spectra were measured on a Varian Mercury-Plus 400 NMR–nuclear magnetic resonance instrument in $CDCl_3$ solution with TMS as internal standard. Infrared spectra were recorded on a Nicolet FTIR 5700 spectrophotometer with KBr pellets. Low-resolution electrospray ionization mass spectra (ESI–MS) were determined with a Finnigan LCQ Advantage Max spectrometer.

Preparation of the title compounds

Preparation of the title compounds is shown in Scheme 1. The 1*H*-pyrazole derivatives were obtained by the condensation of 1,3-diketone compounds with hydrazine monohydrate in ethanol. The 1,3-diketone compounds were prepared from aryl methyl ketones via Claisen condensation with aromatic esters according to the literature methods [4]. The crude products were recrystallized from dilute ethanol solution to give 1*H*-pyrazoles derivatives in yields of 59–80 %.

Preparation of 1,3-diketone compounds

The aryl methyl ketones (0.04 mol) are dissolved in 50 mL toluene and $NaNH_2$ (1.95 g, 0.05 mol) is added. The mixture is stirred at 80 °C for 15 min and the aromatic esters (0.04 mol) are added. The stirring is prolonged for 6 h. The reaction mixture is cooled to room temperature and acidified with dilute hydrochloric acid.



Scheme 1 Synthetic route to compounds **1b–5b**

The toluene layer is separated and the solvent removed by evaporation. The residual solid is recrystallized from ethanol to obtain the 1,3-diketone compounds **1a**–**5a**.

*1-(4-Methylphenyl)-3-(4-chlorophenyl)-propane-1,3-dione (**1a**)* Colorless crystals, yield 78 %, mp 136–137 °C; IR (KBr): *v* 3,469 (w), 3,065 (m), 2,952 (m), 2,860 (w), 1,605 (s), 1,545 (m), 1,509 (s), 1,463 (m), 1,369 (w), 1,231 (s), 1,150 (m), 1,100 (s), 1,021 (s), 856 (s), 798 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 4.61 (s, 0.16H, keto CH_2), 6.78 (s, 1,H, enol CH), 7.06–7.09 (m, 2H), 7.48 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.90 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.99–8.02 (m, 2H), 17.03 (br s,1H, enol OH) ppm; ESI–MS: m/z 273.68 $[M + 1]^+$; Anal. calcd. for $C_{16}H_{13}ClO_2$: C, 70.46; H, 4.80; found C, 70.93; H, 4.75 %.

*1-(4-tert-Butylphenyl)-3-(4-methoxyphenyl)-propane-1,3-dione (**2a**)* Colorless crystals, yield 67 %, mp 82–83 °C; IR (KBr): *v* 3,477 (w), 3,071 (m), 2,972 (s), 2,836 (m), 1,603 (s), 1,547 (m), 1,508 (s), 1,436 (s), 1,307 (m), 1,258 (m), 1,227 (s), 1,168 (s), 1,023 (s), 845 (s), 797 (s), 707 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 9H, $C(CH_3)_3$), 3.89 (s, 3H, OCH_3), 4.58 (s, 0.16H, keto CH_2), 6.79 (s, 1H, enol CH), 6.98 (d, 2H, Ar–H, $J = 8.8$ Hz), 7.50 (d, 2H, Ar–H, $J = 8.8$ Hz), 7.91 (d, 2H, Ar–H, $J = 8.8$ Hz), 7.98 (d, 2H, Ar–H, $J = 8.8$ Hz), 17.10 (br s,1H, enol OH) ppm; ESI–MS: m/z 311.06 $[M + 1]^+$; Anal. calcd. for $C_{20}H_{22}O_3$: C, 77.39; H, 7.14; found C, 77.28; H, 7.11 %.

*1-(4-Phenylphenyl)-3-phenyl-propane-1,3-dione (**3a**)* White powder, yield 62 %, mp 109–110 °C (Ref. [10] 111 °C); IR (KBr): *v* 3,448 (w), 3,055 (w), 2,956 (w), 2,863 (w), 1,596 (s), 1,571 (s), 1,509 (s), 1,483 (s), 1,443 (s), 1,295 (s), 1,226 (s), 1,182 (m), 1,070 (m), 1,004 (m), 852 (s), 755 (s), 685 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.70 (s, 0.19H, keto CH_2), 6.91 (s, 1H, enol CH), 7.41–7.56 (m, 6H), 7.64–7.67 (m, 2H), 7.72 (d, 2H, Ar–H, $J = 8.4$ Hz), 8.00–8.02 (m, 2H), 8.07 (d, 2H, Ar–H, $J = 8.4$ Hz), 16.92 (br s,1H, enol OH) ppm; ESI–MS: m/z 300.95 $[M + 1]^+$; Anal. calcd. for $C_{21}H_{16}O_2$: C, 83.98; H, 5.37; found C, 84.32; H, 5.29 %.

*1-(4-Methylphenyl)-3-(4-fluorophenyl)-propane-1,3-dione (**4a**)* Colorless crystals, yield 72 %, mp 125–126 °C; IR (KBr): *v* 3,452 (w), 3,078 (m), 2,961 (m), 2,870 (w), 1,602 (s), 1,540 (m), 1,505 (s), 1,456 (m), 1,365 (w), 1,226 (s), 1,158 (s), 1,104 (m), 1,011 (m), 850 (s), 794 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 4.56 (s, 0.14H, keto CH_2), 6.78 (s, 1H, enol CH), 7.10–7.13 (m, 2H), 7.50 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.81 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.96–7.99 (m, 2H), 17.06 (br s,1H, enol OH) ppm; ESI–MS: m/z 257.11 $[M + 1]^+$; Anal. calcd. for $C_{16}H_{13}FO_2$: C, 74.99; H, 5.11; found C, 75.46; H, 5.03 %.

*1-(4-Fluorophenyl)-3-(furan-2-yl)-propane-1,3-dione (**5a**)* Pale yellow crystals, yield 76 %, mp 80–81 °C; IR (KBr): *v* 3,426 (w), 3,065 (w), 2,978 (w), 1,604 (s), 1,549 (m), 1,505 (s), 1,467 (s), 1,298 (m), 1,225 (s), 1,161 (s), 1,093 (m), 1,014 (s), 842 (m), 789 (s), 753 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.46 (s, 0.10H, keto

CH_2), 6.59–6.60 (m, 1H), 6.72 (s, 1H, enol CH), 7.14–7.18 (m, 2H), 7.24 (d, 1H, $J = 3.6$ Hz), 7.62 (s, 1H), 7.97–8.00 (m, 2H), 16.20 (br s,1H, enol OH) ppm; ESI–MS: m/z 232.83 $[M + 1]^+$; Anal. calcd. for $C_{13}H_9FO_3$: C, 67.24; H, 3.91; found C, 67.63; H, 3.85 %.

Preparation of 1H-pyrazole derivatives

Hydrazine monohydrate (0.01 mol) in ethanol is added dropwise to a refluxing ethanol solution (30 mL) of the corresponding 1,3-diketone (0.01 mol). The solution is then refluxed for 3 h. After completion of the reaction (detected by thin layer chromatography, TLC), the solvent is removed by evaporation. The residual solid is recrystallized from dilute ethanol solution to give the title compounds **1b**–**5b**.

*3-(4-Chlorophenyl)-5-(4-methylphenyl)-1H-pyrazole (**1b**)* White solid, yield 71 %, mp 199–200 °C; IR: (KBr): , (b, s), 3,053 (m), 2957 (m), 2,856 (m), 1,605 (m), 1,506 (s), 1,467 (s), 1,451 (m), 1,373 (w), 1,258 (s), 1,220 (s), 1,159 (s), 1,039 (s), 978 (s), 798 (s), 755 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.35 (s, 3H, CH_3), 6.81 (s, 1H, pyrazolyl C–H), 7.35–7.40 (m, 2H, Ar–H), 7.50 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.63 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.75–7.7.80 (m, 2H, Ar–H) ppm, pyrazolyl N–H not found; ESI–MS: m/z 269.7 $[M + 1]^+$; Anal. calcd. for $C_{16}H_{13}ClN_2$: C, 71.51; H, 4.88; N, 10.42; found C, 71.86; H, 4.83; N, 10.45 %.

*3(5)-(4-tert-Butylphenyl)-5(3)-(4-methoxyphenyl)-1H-pyrazole (**2b**)* Colorless needles, yield 72 %, mp 185–186 °C; IR: (KBr): 3,205 (b, s), 3,019 (m), 2,956 (s), 2,867 (m), 1,615 (s), 1,504 (s), 1,463 (s), 1,245 (s), 1,175 (s), 1,036 (s), 970 (s), 837 (s), 792 (s), 736 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 1.34 (9H, s, $C(CH_3)_3$), 3.83 (3H, s, CH_3O), 6.73 (1H, s, pyrazloyl C–H), 6.91 (2H, d, Ar–H, $J = 8.4$ Hz), 7.42 (2H, d, Ar–H, $J = 8.0$ Hz), 7.64–7.67 (4H, m, Ar–H), 8.20 (1H, bs, N–H) ppm; ESI–MS: m/z 612.7 $[2\ M]^+$, 306.2 $[M + 1]^+$; Anal. calcd. for $C_{20}H_{22}N_2O$: C, 78.40; H, 7.24; N, 9.14; found C, 78.21; H, 7.20; N, 9.26 %.

*3-(4-Phenylphenyl)-5-phenyl-1H-pyrazole (**3b**)* White solid, yield 80 %, mp 206–207 °C; IR: (KBr): 3,220 (b, s), 3,030 (m), 3,001 (m), 1,596 (m), 1,487 (s), 1,459 (s), 1,178 (m), 1,053 (m), 968 (s), 840 (s), 801 (s), 761 (s), 691 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.91 (1H, s, pyrazloyl C–H), 7.35–7.48 (6H, m, Ar–H), 7.60–7.65 (4H, m, Ar–H), 7.76 (2H, d, Ar–H, $J = 7.6$ Hz), 7.82 (2H, d, Ar–H, $J = 8.0$ Hz) ppm, N–H not found; ESI–MS: m/z 297.3 $[M + 1]^+$; Anal. calcd. for $C_{21}H_{16}N_2$: C, 85.11; H, 5.44; N, 9.45; found C, 85.36; H, 5.29; N, 9.38 %.

*3-(4-Fluorophenyl)-5-(4-methylphenyl)-1H-pyrazole (**4b**)* Colorless needles, yield 67 %, mp 190–191 °C; IR: (KBr): 3,186 (b, s), 3,060 (m), 2,964 (m), 2,868 (m), 1,607 (m), 1,510 (s), 1,471 (s), 1,445 (m), 1,360 (w), 1,258 (m), 1,227 (s), 1,155 (s), 1,043 (s), 981 (s), 804 (s), 746 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 6.80 (s, 1H, pyrazolyl C–H), 7.05–7.10 (m, 2H, Ar–H), 7.48 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.60 (d, 2H, Ar–H, $J = 8.4$ Hz), 7.68–7.72 (m, 2H, Ar–H) ppm,

pyrazolyl N–H not found; ESI–MS: m/z 253.2 $[M + 1]^+$; Anal. calcd. for $C_{16}H_{13}FN_2$: C, 76.17; H, 5.19; N, 11.10; found C, 76.46; H, 5.11; N, 11.35 %.

*3-(4-Fluorophenyl)-5-(furan-2-yl)-1H-pyrazole (**5b**)* White solid, yield 59 %, mp 164–165 °C; IR: (KBr): 3,147 (b, s), 3,066 (s), 2,993 (m), 2,871 (m), 1,613 (s), 1,509 (s), 1,462 (m), 1,430 (s), 1,233 (s), 1,168 (s), 1,075 (s), 1,011 (s), 894 (s), 837 (s), 787 (s), 730 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.15 (1H, bs, N–H), 6.48 (1H, s, pyrazloyl C–H), 6.68 (1H, d, furfural C–H, $J = 2.8$ Hz), 7.08–7.12 (2H, m, Ar–H), 6.72 (1H, s, furfural C–H), 7.43 (1H, s, furfural C–H), 7.70–7.74 (2H, m, Ar–H) ppm; ESI–MS: m/z 229.1 $[M + 1]^+$; Anal. calcd. for $C_{13}H_9FN_2O$: C, 68.41; H, 3.97; N, 12.27; found C, 68.16; H, 3.92; N, 12.16 %.

Crystal structure determination

A single crystal of compound **2b** suitable for X-ray diffraction analysis was obtained by slow evaporation from CH_2Cl_2–EtOH (1:2) solutions. A colorless crystal having dimensions of 0.20 mm × 0.10 mm × 0.10 mm was mounted on the top of the glass fibers. The data were collected at 298 (2) K on a Bruker Smart 1000 CCD diffractometer using graphite monochromatic Mo Kα radiation ($\lambda = 0.71073$ Å). The intensity data were corrected for *Lp* factors and empirical. The structure was solved by direct methods with the SHELXTL-97 program [11]. The final refinement was made by full-matrix least-squares techniques with anisotropic thermal parameters for the non-hydrogen atoms on F^2. All the H atoms were added according to the theoretical models. Multi-scan absorption correction was applied by use of the SADABS program [12]. A summary of crystal data is presented in Table 1.

Results and discussion

Spectral characterization

Compounds **1a**–**5a** and **1b**–**5b** were characterized by elemental analysis, FTIR, ^1H NMR, and mass spectroscopy. The IR spectra of compounds **1a**–**5a** showed that the strong absorption bands in the regions of 1,605–1,596 cm^{-1} and 1,509–1,505 cm^{-1} belonged to the C=O and enolic C=C stretching vibrations, respectively. The enolic C–O stretching absorption was observed at 1,225–1,231 cm^{-1}. These bands confirmed the presence of the keto-enol tautomer of the 1,3-diketone compounds. The IR spectra of compounds **1b**–**5b** exhibited broad bands around 3,220–3,147 cm^{-1} due to N–H stretching vibrations, strong absorption bands in the region of 1,618–1,596 cm^{-1} were assigned to the C=N stretching vibrations, and strong absorption bands at 1,513–1,487 cm^{-1} were attributed to the N–H bending vibrations. Medium bands in the range of 1,075–1,036 cm^{-1} were due to N–N stretching vibrations [13, 14].

Table 1 Crystal data and structure refinements for compound **2b**

Structural data	Value
Compound	**2b**
Empirical formula	$C_{20}H_{22}N_2O$
Formula weight	306.40
Temperature (K)	298 (2)
Crystal system	Triclinic
Space group	*P*-1
a (Å)	9.876 (6)
b (Å)	13.559 (8)
c (Å)	14.095 (8)
α (°)	85.706 (12)
β (°)	74.174 (11)
γ (°)	73.273 (10)
Volume (Å^3)	1,739.1 (18)
Z	4
Density (calc.) (g cm^{-3})	1.170
Absorption coefficient (mm^{-1})	0.073
F(000)	656
Crystal size (mm^3)	0.20 × 0.10 × 0.10
Theta range for data collection (°)	1.50–25.00
h/*k*/*l*	−11, 11/−16, 15/−13, 16
Reflections collected	19,036
Independent reflections	6,043[$R_{(int)} = 0.0580$]
Data/restraints/parameters	6,043/0/425
Goodness-of-fit on F^2	1.455
Final *R* indices [$I > 2\sigma(I)$]	$R^1 = 0.1484$ $wR^2 = 0.3926$
R indices (all data)	$R^1 = 0.2154$ $wR^2 = 0.4299$
Largest diff. peak and hole (e Å^{-3})	0.536 and −0.356

The ^{1}H NMR spectra of compounds **1a**–**5a** showed that the single peaks at $\delta = 16.20$–17.10 ppm were due to the enolic OH protons, the single peaks at $\delta = 6.72-6.91$ ppm were assigned to the vinylic protons in enol and the single peaks at $\delta = 4.46-4.70$ ppm were attributed to the keto-CH_2 protons. These were consistent with the results of the IR spectra for the 1,3-diketone compounds. The ^{1}H NMR spectra of compounds **1b**–**5b** displayed the aromatic protons at $\delta = 6.68$–7.82 ppm, and exhibited a typical proton chemical shift of 3,5-disubstituted pyrazole (4–H) at $\delta = 6.48$–6.91 ppm. On the other hand, the N–H resonance of the pyrazolyl ring of compounds **2b** and **5b** appeared as a broad and flat signal at $\delta = 6.15$–6.73 ppm, but that of compounds **1b**, **3b**, and **4b** were not observed in $CDCl_3$. Apparently, there is a fast tautomerism of the 1*H*-pyrazoles in $CDCl_3$ solution. This is in accordance with the result in the literature [15].

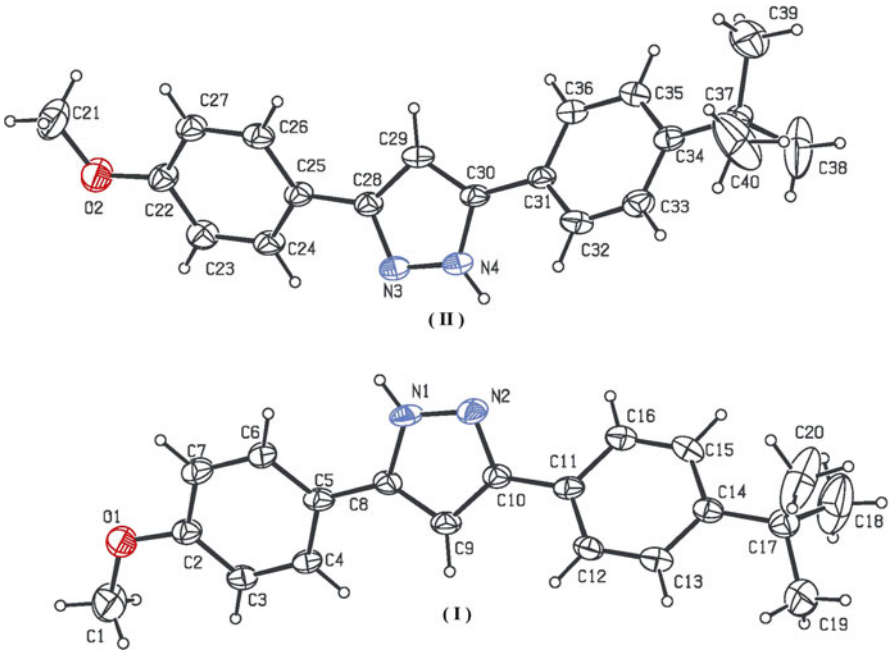


Fig. 1 View of compound **2b** (tautomers **I** and **II**) with the atom-labeling scheme and 50 % probability displacement ellipsoids

X-ray crystal structure

The crystal structure of compound **2b** contains a dimer formed by one tautomer **I** and the other tautomer **II** [16, 17]. Figure 1 shows labeled displacement ellipsoid plots of these two tautomers, and the selected bond lengths, bond angles and torsion angles are summarized in Table 2. The pyrazole moiety in both tautomers is nearly coplanar from the torsion angles N1–C8–C9–C10, C8–C9–C10–N2, C9–C8–N1–N2, C9–C10–N2–N1 and C8–N1–N2–C10 in tautomer **I**, and N3–C28–C29–C30, C28–C29–C30–N4, C29–C28–N3–N4, C29–C30–N4–N3 and C28–N3–N4–C30 in tautomer **II** (Table 2). The dihedral angles formed by two benzene rings (C2–C7) and (C11–C16) with the pyrazole ring are 26.59° and 28.10° for **I**, respectively, and those of two benzene rings (C22–C27) and (C31–C36) with the pyrazole ring are 27.00° and 25.86° for **II**, respectively. But the two pyrazole rings in tautomers **I** and **II** are close to a planar and their dihedral angle is 4.03°, which leads to a strong intermolecular hydrogen bond in the dimeric structure.

In the structure of compound **2b**, the strong intermolecular hydrogen bonds are the primary factors in building of crystal network. The hydrogen-bonding geometric parameters are listed in Table 3. The network is connected by the two kinds of N–H···N hydrogen bonds to form cyclic dimers containing the tautomers **I** and **II** (Fig. 2). The first N–H···N interaction is from N1 to N3 [N1···N3 = 2.813 (3) Å, N1–H1···N3 = 132 (3)°], and the second is between N4 and N2 [N4···N2 = 2.837 (3) Å, N4–H4A···N2 = 131 (3)°]. Obviously, compound **2b** packs via neutral

Table 2 Selected geometric parameters for compound **2b**

Parameter	Values		
Bond lengths (Å)			
C(5)–C(8)	1.443(8)	C(25)–C(28)	1.462(8)
C(8)–N(1)	1.347(7)	C(28)–N(3)	1.332(7)
C(8)–C(9)	1.405(8)	C(28)–C(29)	1.393(8)
C(9)–C(10)	1.386(8)	C(29)–C(30)	1.388(8)
C(10)–N(2)	1.334(7)	C(30)–N(4)	1.353(7)
C(10)–C(11)	1.474(8)	C(30)–C(31)	1.455(8)
N(1)–N(2)	1.347(6)	N(3)–(4)	1.330(6)
Angles (°)			
N(1)–C(8)–C(9)	106.0(5)	N(3)–C(28)–C(29)	108.0(5)
N(1)–C(8)–C(5)	120.4(5)	N(3)–C(28)–C(25)	120.4(5)
C(9)–C(8)–C(5)	133.6(5)	C(29)–C(28)–C(25)	131.6(5)
C(10)–C(9)–C(8)	106.3(5)	C(30)–C(29)–C(28)	106.5(5)
N(2)–C(10)–C(9)	109.1(5)	N(4)–C(30)–C(29)	106.3(5)
N(2)–C(10)–C(11)	119.8(5)	N(4)–C(30)–C(31)	120.3(5)
C(9)–C(10)–C(11)	131.1(5)	C(29)–C(30)–C(31)	133.4(5)
C(12)–C(11)–C(10)	122.3(5)	C(32)–C(31)–C(30)	121.7(5)
C(16)–C(11)–C(10)	121.5(6)	C(36)–C(31)–C(30)	121.5(5)
C(8)–N(1)–N(2)	110.9(5)	N(4)–N(3)–C(28)	108.8(5)
C(10)–N(2)–N(1)	107.7(5)	N(3)–N(4)–C(30)	110.3(5)
Torsion angles (°)			
N(1)–C(8)–C(9)–C(10)	0.7(4)	N(3)–C(28)–C(29)–C(30)	0.6(6)
C(8)–C(9)–C(10)–N(2)	−0.8(6)	C(28)–C(29)–C(30)–N(4)	−0.9(6)
C(9)–C(8)–N(1)–N(2)	−0.3(6)	C(29)–C(28)–N(3)–N(4)	0.0(6)
C(9)–C(10)–N(2)–N(1)	0.6(6)	C(29)–C(30)–N(4)–N(3)	0.9(6)
C(8)–N(1)–N(2)–C(10)	−0.2(6)	C(28)–N(3)–N(4)–C(30)	−0.5(6)

Table 3 Hydrogen-bonding geometry for compound **2b** (Å, °)

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(1)···N(3)	0.86 (3)	2.16 (3)	2.813 (3)	132 (3)
N(4)–H(4A)···N(2)	0.86 (3)	2.20 (3)	2.837 (3)	131 (3)

N–H···N bonds which are assisted by resonance through the ···N=C–C=C–NH··· iminoenamine π–conjugated system [18].

Conclusion

To summarize, we prepared some new 1*H*-pyrazole derivatives from aryl methyl ketones via Claisen condensation with aromatic esters, followed by cyclization with

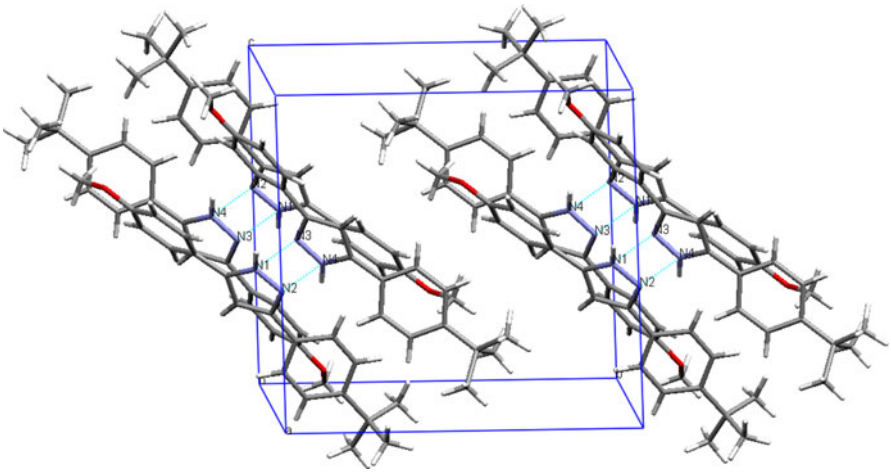


Fig. 2 View for the packing of the dimeric structure in compound **2b**. *Dotted lines* indicate intermolecular N–H···N hydrogen bonds

hydrazine monohydrate in ethanol. Their structures were established on the basis of elemental analysis, FTIR, ^{1}H NMR and mass spectroscopy. And the crystal structure of compound **2b** was confirmed by X-ray crystallographic studies. The results showed that its crystal structure exists as tautomers **I** and **II**, and its molecules are connected by the N–H···N intermolecular hydrogen bonds to form cyclic dimers consisting the tautomers **I** and **II**.

Supplementary materials

CCDC reference number 711754 contains the supplementary crystallographic data for this article. This data can be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; email: deposit@ccdc. cam.ac.uk or http://www.ccdc.cam.ac.uk.).

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