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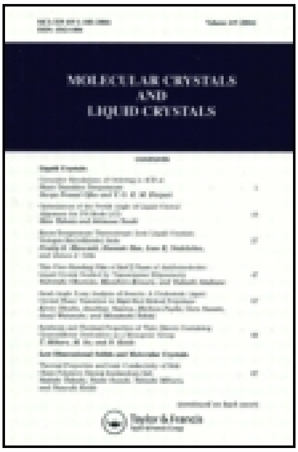

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Synthesis, Characterization, and Crystal Structures of N′^{2},N′^{6}-Bis(benzylidene) pyridine-2,6-Dicarbohydrazide Derivatives

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Synthesis, Characterization, and Crystal Structures of N′2,N′6-Bis(benzylidene) pyridine-2,6-Dicarbohydrazide Derivatives

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N′2,N′6-bis(m-nitrobenzylidene)pyridine-2,6-dicarbohydrazid (***a***), *N′2,N′6-bis(p-nitrobenzylidene)pyridine-2,6-dicarbohydrazid* (***b***), *and N′2,N′6-bis(p-chlorobenzylidene) pyridine-2,6-dicarbohydrazid* (***c***) *were synthesized and characterized by ^{1}H NMR, Mass Spectroscopy, and Infrared Spectroscopy. The single crystals of compound* $C_{27}H_{29}N_9O_{11}$ (***1***), $C_{27}H_{29}N_9O_{11}$ (***2***), *and* $C_{21}H_{15}Cl_2N_5O_4$ (***3***) *were characterized by X-ray single-crystal diffraction analysis. The crystal structure analysis revealed that compound* ***1*** *crystallizes in a monoclinic system, space group C2/c, a = 24.6504(10) Å, b = 10.4624(6) Å, c = 14.4850(6) Å. The compound* ***2*** *crystallizes in monoclinic system, space group C2/c, a = 24.6505(9) Å, b = 10.4618(4) Å, c = 14.4946(5) Å. The compound* ***3*** *crystallizes in a monoclinic system, space group P2 (1)/n, a = 8.6377(9) Å, b = 14.4815(15) Å, c = 17.6598(19) Å.*

Keywords Crystal structure; hydrazone; pyridine-2,6-dicarbohydrazid; synthesis

1. Introduction

During the past decades, special attention has been paid to hydrazone derivatives owing to their diverse biological activities, strong coordination ability, and various coordination forms [1–4], and researchers found that hydrazone compounds possess various biological activities including antibacterial [5, 6], anti-inflammatory [7], and anticancer activity [8, 9]. These research works are beneficial to expand the application of hydrazone compounds in pharmaceutical, pesticide, materials, and analysis areas. In this paper, N′2,N′6-bis(m-nitrobenzylidene)pyridine-2,6-dicarbohydrazid [10], N′2,N′6-bis (p-nitrobenzylidene)pyridine-2,6-dicarbohydrazid, and N′2,N′6-bis(p-chlorobenzylidene) pyridine-2,6-dicarbohydrazid were synthesized, and characterized by ^{1}H NMR, mass spectroscopy (MS), and infrared spectroscopy (IR). Their crystal structure was characterized by X-ray single-crystal diffraction analysis.

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Table 1. Crystal data and refinement parameters for the compounds

Compound	**1**	**2**	**3**
CCDC number	797507	807624	807051
Empirical formula	$C_{27}H_{29}N_9O_{11}$	$C_{27}H_{29}N_9O_{11}$	$C_{21}H_{15}C1_2N_5O_4$
Formula weight	655.59	655.59	472.28
Temperature (K)	296(2)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal size (mm^3)	0.50 × 0.40 × 0.25	0.50 × 0.35 × 0.30	0.50 × 0.37 × 0.31
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/*c*	C2/*c*	P2(1)/*n*
(a)/Å	24.6504(10)	24.6505(9)	8.6377(9)
(b)/Å	10.4624(6)	10.4618(4)	14.4815(15)
(c)/Å	14.4850(6)	14.4946(5)	17.6598(19)
α (°)	90	90	90
β (°)	120.360(2)	120.4070(10)	97.683(3)
γ (°)	90	90	90
V (Å^3)	3223.4(3)	3223.8(2)	2189.2(4)
Z	4	6	4
D_{calc} (g/cm^3)	1.351	1.351	1.433
μ (mm^{-1})	0.107	0.107	0.335
F (000)	1368	1368	968
θ range (°)	2.17–26.01	1.92–26.01	1.83–25.00
Range/indices (h, k, l)	−30/30, −12/12, −17/17	−23/30, −12/12, −17/13	−10/10, −17/17, −20/20
Reflections collected/unique	17146/3169	10700/3143	14501/3837
Max. and min. transmission	0.9737 and 0.9484	0.9686 and 0.9484	0.9032 and 0.8503
Data/restraints/parmeters	3169/0/220	3143/0/221	3837/0/298
Goodness-of-fit on F^2	1.224	1.261	1.075
R_1, wR_2 [$I > 2\sigma$ (I)] [a]	0.0825, 0.2730	0.0846, 0.2774	0.0654, 0.1440
R_1, wR_2 (all data)	0.0964, 0.2961	0.1016, 0.3081	0.2353, 0.1970
Largest diff.peak and hole (e.Å^{-3})	0.932 and – 0.321	0.966 and –0.383	0.539 and −0.473

[a] $R = \sum ||F_0| - |F_c|| / \sum |F_0|,\ wR_2 = \left[\sum\left[w\left(F_0^2 - F_c^2\right)^2\right] / \sum\left[w\left(F_0^2\right)^2\right]\right]^{1/2}$.

2. Experimental

All reagents for syntheses and analyses were of analytical grade and were purchased from commercial suppliers. The infrared spectra were recorded on a PerkinElmer spectrophotometer in the range of 4000–400 cm^{-1} using the KBr disk technique. The ^{1}H NMR spectra was measured on a Varian-400 MHz spectrometer and mass spectra were recorded on an Agilent 1100 mass spectrometer.

2.1 Synthesis of N'^2,N'^6-Bis(m-nitrobenzylidene)pyridine-2,6-Dicarbohydrazid (a)

Pyridine-2,6-dicarbohydrazid (0.50 g, 2.5 mmol), m-nitrobenzaldehyde (1.14 g, 7.5 mmol), and anhydrous ethanol (30 mL) were added to a three-necked round-bottomed flask under stirring. Then, anhydrous acetic acid (1 mL) was added to the solution. The reaction solution was refluxed for 10 h at 80°C. After cooling, the precipitate was collected, washed with anhydrous ethanol, and dried for 24 h, and a white solid was obtained, with a yield of 85.5%. ^{1}H NMR (400 MHz, DMSO) δ/ppm: 12.58 (s, 2H, NH–N), 8.91 (s, 2H, CH=N), 8.66 (s, 2H, pyridine protons), 8.32 (d, 1H, J = 7.2 Hz, pyridine protons), 7.82 (dd, 6H, J = 8 Hz, J = 16 Hz, aromatic protons), 7.82(m, 2H, aromatic protons). IR (KBr, cm^{-1}):

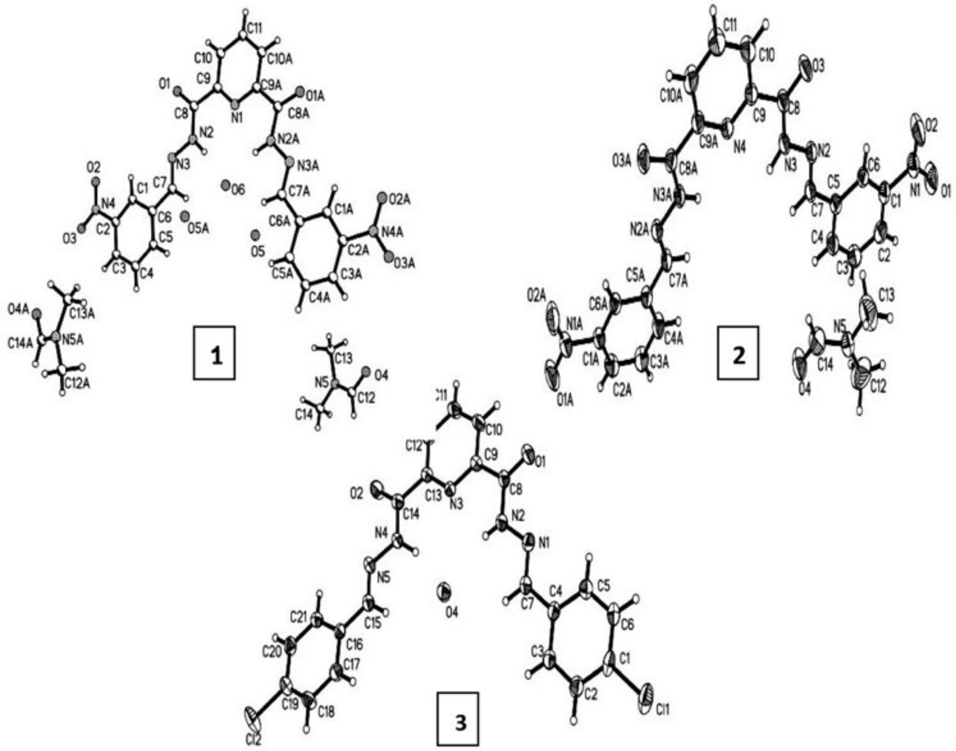

Figure 1. Molecular structure and atom labeling of the compounds **1, 2,** and **3**.

3076, 1669, 1618, 1457, 1351. MS (ESI) *m/z* (%): 460 (M-1, 17), 920 (2(M-1), 100), 922 (2M, 41).

2.2 N'^2,N'^6-Bis(p-nitrobenzylidene)pyridine-2,6-Dicarbohydrazid (b)

Compound **b** was prepared by a similar procedure as that described for **a**, with m-nitrobenzaldehyde replaced by p-nitrobenzaldehyde (1.14 g, 7.5 mmol), and a white solid was obtained, with a yield of 87.6%. ^{1}H NMR (400 MHz, DMSO) δ/ppm: 12.58 (s, 2H, NH–N), 8.91 (s, 2H, CH=N), 8.66 (s, 2H, pyridine protons), 8.40 (d, 1H, $J = 7.2$ Hz, pyridine protons), 8.33 (d, 6H, $J = 7.2$ Hz, aromatic protons), 7.82 (m, 2H, aromatic protons). IR (KBr, cm^{-1}): 3075, 1683, 1619, 1451, 1351. MS (ESI) *m/z* (%): 460 (M-1, 18), 920 (2(M-1), 100), 922 (2M, 44).

2.3 N'^2,N'^6-Bis(p-chlorobenzylidene)pyridine-2,6-Dicarbohydrazid (c)

Compound **c** was prepared by a similar procedure as that described for **a**, with m-nitrobenzaldehyde replaced by p-chlorobenzaldehyde (1.10 g, 7.5 mmol), and a white solid was obtained, with a yield of 85.4%. ^{1}H NMR (400 MHz, DMSO) δ/ppm: 12.39 (s, 2H, NH—N), 8.78(s, 2H, CH=N), 8.36 (d, 1H, $J = 7.2$ Hz, pyridine protons), 8.28(m, 1H, pyridine protons), 7.85(d, 4H, $J = 8.4$ Hz, aromatic protons), 7.57 (d, 4H, $J = 8.4$ Hz, aromatic protons). IR (KBr, cm^{-1}): 3050, 1664, 1591, 1490, 839. MS (ESI) *m/z* (%): 438 (M-1, 10), 878 (2M, 100), 922 (2(M-1), 61).

Table 2. Selected bond lengths [Å] and angles [deg] for compounds **1, 2,** and **3**

1		2		3	
		Bond lengths			
N1–C9	1.321 (3)	C1–C6	1.371 (4)	N1–C7	1.261 (4)
N2–C8	1.339 (3)	C1–N1	1.478 (4)	N1–N2	1.367 (5)
N2–N3	1.357 (3)	C5–C6	1.404 (4)	N2–C8	1.338 (4)
N2–H2	0.860 (4)	C5–C7	1.455 (4)	N2–H2	0.760 (4)
N3–C7	1.269 (3)	C7–N2	1.273 (3)	N3–C9	1.345 (4)
N4–O2	1.207 (4)	C8–O3	1.220 (3)	O1–C8	1.221 (4)
N4–C2	1.479 (4)	C8–N3	1.345 (3)	C1–C2	1.377 (6)
O1–C8	1.225 (3)	C8–C9	1.496 (4)	C2–C3	1.374 (7)
C1–C2	1.371 (3)	C9–N4	1.325 (3)	C3–C4	1.393 (5)
C1–C6	1.396 (3)	N1–O1	1.208 (4)	C4–C7	1.453 (6)
C6–C7	1.456 (3)	N2–N3	1.372 (3)	C8–C9	1.473 (6)
C8–C9	1.494 (3)	N3–H3	0.900 (4)	C1–Cl1	1.733 (5)
		Bond angles			
C8–N2–N3	119.2 (2)	C6–C5–C7	122.6 (2)	C7–N1–N2	116.5 (4)
C8–N2–H2	128 (2)	C1–C6–C5	117.9 (3)	C8–N2–N1	118.4 (4)
N3–N2–H2	113 (2)	C1–C6–H6	121.0	C8–N2–H2A	120 (3)
C7–N3–N2	115.9 (2)	C5–C6–H6	121.0	N1–N2–H2	122 (3)
O3–N2–O2	123.0 (3)	N2–C7–C5	122.1 (2)	C2–C1–Cl1	118.8 (3)
O2–N4–C2	119.0 (3)	N2–C7–H7	118.9	C3–C2–C1	118.5 (4)
C2–C1–C6	117.8 (2)	C5–C7–H7	118.9	C3–C2–H2	120.8
C2–C1–H1	121.1	O3–C8–N3	123.9 (2)	C2–C3–C4	119.4
C6–C1–H1	121.1	O3–C8–C9	121.2 (2)	C2–C3–H3	119.4
C1–C2–N4	117.5 (3)	N3–C8–C9	114.9 (2)	C3–C4–C7	119.8 (4)
C1–C6–C7	122.6 (2)	N4–C9–C8	119.3 (2)	N1–C7–C4	120.7 (4)
N3–C7–C6	122.2 (2)	C10–C9–C8	118.1 (2)	N1–C7–H7	119.7
N3–C7–H7	118.9	C11–C10–H10	120.9	C4–C7–H7	119.7
C6–C7–H7	118.9	C7–N2–N3	115.6 (2)	O1–C8–N2	123.8 (5)
O1–C8–N2	123.8 (2)	C8–N3–N2	118.9 (2)	O1–C8–C9	121.5 (3)
O1–C8–C9	121.1 (2)	C8–N3–H3A	129 (2)	N2–C8–C9	114.7 (3)
N1–C9–C8	119.3 (2)	N2–N3–H3A	112 (2)	N3–C9–C8	119.3 (3)
		Bond angles			
C8–N2–N3	119.2 (2)	C6–C5–C7	122.6 (2)	C7–N1–N2	116.5 (4)
C8–N2–H2	128 (2)	C1–C6–C5	117.9 (3)	C8–N2–N1	118.4 (4)
N3–N2–H2	113 (2)	C1–C6–H6	121.0	C8–N2–H2A	120 (3)
C7–N3–N2	115.9 (2)	C5–C6–H6	121.0	N1–N2–H2	122 (3)
O3–N2–O2	123.0 (3)	N2–C7–C5	122.1 (2)	C2–C1–Cl1	118.8 (3)
O2–N4–C2	119.0 (3)	N2–C7–H7	118.9	C3–C2–C1	118.5 (4)
C2–C1–C6	117.8 (2)	C5–C7–H7	118.9	C3–C2–H2	120.8
C2–C1–H1	121.1	O3–C8–N3	123.9 (2)	C2–C3–C4	119.4
C6–C1–H1	121.1	O3–C8–C9	121.2 (2)	C2–C3–H3	119.4
C1–C2–N4	117.5 (3)	N3–C8–C9	114.9 (2)	C3–C4–C7	119.8 (4)
C1–C6–C7	122.6 (2)	N4–C9–C8	119.3 (2)	N1–C7–C4	120.7 (4)
N3–C7–C6	122.2 (2)	C10–C9–C8	118.1 (2)	N1–C7–H7	119.7
N3–C7–H7	118.9	C11–C10–H10	120.9	C4–C7–H7	119.7
C6–C7–H7	118.9	C7–N2–N3	115.6 (2)	O1–C8–N2	123.8 (5)
O1–C8–N2	123.8 (2)	C8–N3–N2	118.9 (2)	O1–C8–C9	121.5 (3)

Crystals suitable for X-ray diffraction were obtained from the solvent dimethylformamide (DMF) by slow evaporation at room temperature, and single crystals of the compounds **a, b,** and **c** were obtained after a few days.

2.4 X-Ray Crystallographic Study of the Compounds

The single-crystal X-ray diffraction measurement was carried out on a Bruker Smart 1000 CCD area detector. Intensities of reflections were measured using graphite-monochromatized Mo Ka radiation ($\lambda = 0.71073$ Å) with ω scan mode at 296(2) K in the range of $2.60 < \theta < 27.32°$. The structure was identified by direct method and non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-square methods on F^2 by SHELXL-97 program package [11].

3. Results and Discussion

X-ray single-crystal structural analysis indicates that the compound **1** crystallizes in monoclinic system, space group C2/c, $a = 24.6504(10)$ Å, $b = 10.4624(6)$ Å, $c = 14.4850(6)$ Å, $\alpha = 90°$, $\beta = 120.360(2)°$, $\gamma = 90°$, V = 3223.4(3) Å^3, Z = 4. The compound **2** crystallizes in monoclinic system, space group C2/c, $a = 24.6505(9)$ Å, $b = 10.4618(4)$ Å, $c = 14.4946(5)$ Å. The compound **3** crystallizes in monoclinic system, space group P2 (1)/n, $a = 8.6377(9)$ Å, $b = 14.4815(15)$ Å, $c = 17.6598(19)$ Å. The details of the crystallographic data are summarized in Table 1. The view of the compounds' molecular structure with atoms labeling are shown in Fig. 1. The selected bond lengths and angles are listed in Table 2.

In the crystal structure of compound **1** and compound **2**, there are two spacer units (one is from atom C1 to C6, another is from C1A to C6A; one is from atom C1 to C6, another is from C1A to C6A, respectively) that adopt a nearly planar all-*trans* conformation, all the

Table 3. Hydrogen bonds for the compounds **1, 2,** and **3** (Å and °)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (Å)
		1		
N(2)–H(2)···O(6)	0.87 (3)	2.06 (3)	2.913 (3)	169 (3)
C(7)–H(7)···O(6)	0.93	2.48	3.282 (3)	145
C(12)–H(12C)···O(3)	0.96	2.59	3.541 (8)	171
		2		
N(3)–H(3A)···O(5)	0.90 (3)	2.03 (4)	2.913 (3)	168 (3)
C(7)–H(7)···O(5)	0.93	2.47	3.282 (3)	145
		3		
N(2)–H(2A)···O(4)	0.77 (3)	2.35 (3)	3.077 (4)	159 (3)
N(2)–H(2A)···N(3)	0.77 (3)	2.35 (4)	2.694 (5)	109 (3)
N(4)–H(4A)···O(4)	0.93 (7)	2.14 (6)	3.015 (5)	158 (4)
N(4)–H(4A)···N(3)	0.93 (7)	2.36 (4)	2.699 (4)	101 (4)
C(2)–H(2)···O(1)	0.93	2.60	3.471 (5)	157
C(7)–H(7)···O(4)	0.93	2.55	3.355 (5)	145
C(15)–H(15)···O(4)	0.93	2.56	3.366 (5)	145

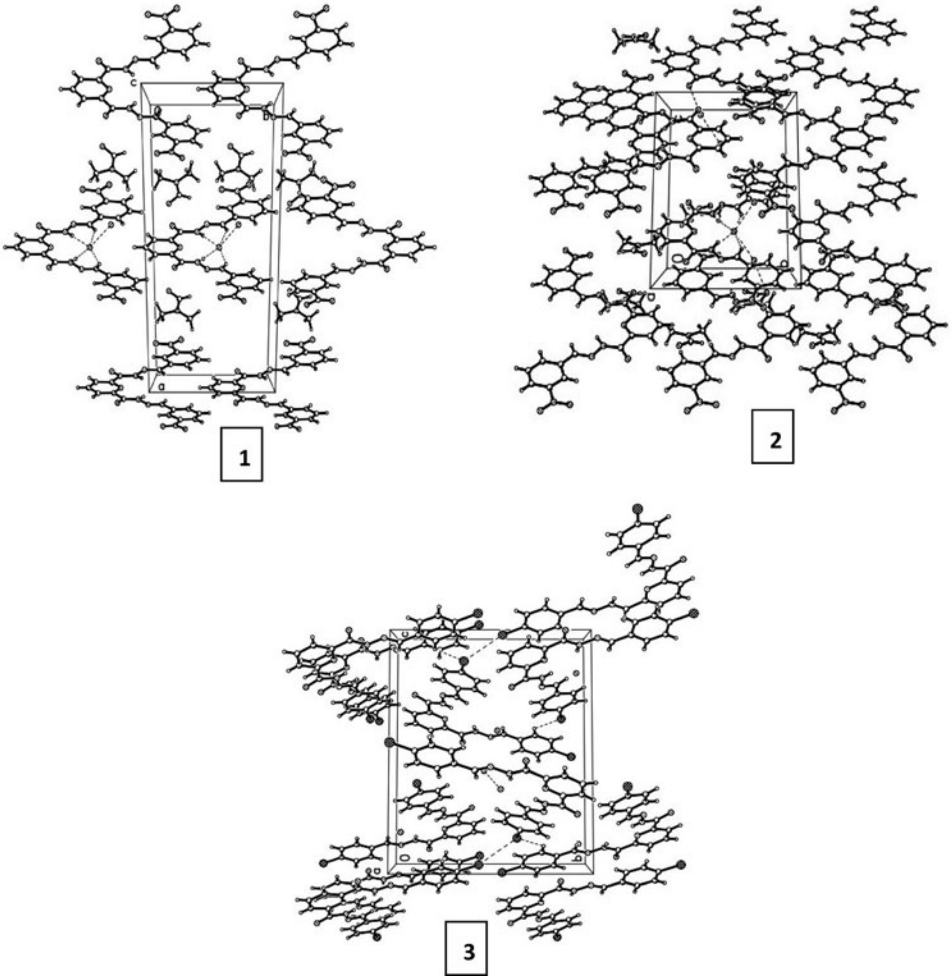

Figure 2. The crystal packing of compounds **1**, **2,** and **3**.

H atoms bonded to C atoms were set to the ideal geometrical position with C–H ranging from 0.93 Å to 0.96 Å. The plane of the pyridine ring is nearly coplanar with the planes of the benzene ring, and the maximum dihedral angle of compounds **1, 2** does not exceed 3.2°and 4.2°, respectively. In the crystal structure of compound **3**, all the H atoms bonded to C atoms were set to the ideal geometrical position with C–H 0.93 Å. The plane of pyridine ring is not nearly coplanar with the planes of the benzene ring, with the maximum of the dihedral angle being in excess of 9.4°.

The hydrogen bonds for the compounds **1, 2,** and **3** (Å, deg) are listed in Table 3. Two intramolecular hydrogen bonds [N—H···O6, C–H···O6] were observed in the compound **1** and compound **2**, respectively. There is one intermolecular hydrogen bond between the hydrogen atom of the DMF (C12···H12) and the oxygen atom of the nitryl (O3) in compound **1** with the C12···O3 distance of 3.541(8). Six intramolecular hydrogen bonds were observed in compound **3**. The length of the hydrogen bonds N–H···O and C···H···O of compound **1** are 2.913(3) Å and 3.282(3) Å, respectively, which are equal to that of compound **2,** but less than that of compound **3**.

In the crystal structures of compound **1** and compound **2**, **a** molecules and **b** molecules are located in the same plane, linked by the DMF molecule through intermolecular hydrogen bonds, forming packing structures. In the crystal structures of compound **3**, **c** molecules are not located in the same plane, linked by intermolecular hydrogen bonds, forming packing structures (Fig. 2).

4. Conclusion

N'^2,N'^6-bis(m-nitrobenzylidene)pyridine-2,6-dicarbohydrazid, N'^2,N'^6-bis(p-nitrobenzylidene) pyridine- 2, 6- dicarbohydrazid, and N'^2,N'^6-bis (p- chlorobenzylidene) pyridine- 2,6-dicarbohydrazid were synthesized and characterized by ^{1}H NMR, mass spectroscopy, and infrared spectroscopy. The crystals of compounds **1**, **2**, and **3** were grown in the solvent DMF at room temperature, and they all crystallize in the monoclinic system. In the crystal structures of compounds **1**, **2,** and **3**, the adjacent two molecules are linked by intermolecular hydrogen bonds and intramolecular hydrogen bonds, forming packing structures. The maximum dihedral angle of compounds **1** and **2** is less than that of compound **3**.

Supplementary Material

CCDC 797507, 807624, and 807051 contain the supplementary crystallographic data for this paper. These data can be obtained from The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk.

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