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Molecular structure of di-aryl-aldimines by multinuclear magnetic resonance and X-ray diffraction

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Abstract

The complete ^{1}H, ^{13}C and ^{15}N NMR analyses for a series of 25 diaryl-aldimines containing phenyl, pyridyl, pyrazolone and furanyl moieties are described herein. Detailed evaluation of substituent chemical shift and coupling constant effects showed that interaction between the lone pair of the pyrazolone carbonyl group or the nitrogen of 2-substitued pyridines with the aldimine hydrogen increases the $^{1}J_{CH}$ value and shifts the resonance signal for this hydrogen to high frequency, in the ^{1}H NMR spectra. The X-ray crystal structure analysis of pyrazolone substituted aldimines evidenced the planarity of the aryl groups which are conjugated with the C=N double bond. In the case of the *N*-(2-pyridinemethylene)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one, two rotamers were observed in the same unit cell.

Keywords: ^{1}H; ^{13}C; ^{15}N NMR; Aldimine; Weak interactions; X-ray

1. Introduction

Since aldimines were first synthesized in 1964 [1], there has been a continued interest in the study of compounds possessing carbon–nitrogen double bonds due to the fact that they are precursors of substances [2] with biological activity, as well as stable and useful intermediates for the synthesis of other substrates.

Carbon–carbon double bond systems having donor and acceptor groups on opposite sides of the molecules [3] exhibit the 'push–pull effect' and have been widely recognized as important candidates for applications in the field of nonlinear optics. They have been analyzed primarily by vibrational and electronic spectroscopy [4]. From the NMR point of view, the 'push–pull' concept has been used to account for their unusual ^{13}C chemical shifts, where one of the signals is shifted to high and the other to low frequency [5]. These shifts are associated with a redistribution of the electronic charge in the ethylenic carbons and a decrease of the rotational barrier of the C=C double bond [6].

The structure and spectroscopy data for a series of 25 aldimines containing phenyl or heterocyclic substituents conjugated with the C=N double bond (Scheme 1) were analyzed using multinuclear magnetic resonance and monocrystal X-ray diffraction. The compounds described herein possess an iminic

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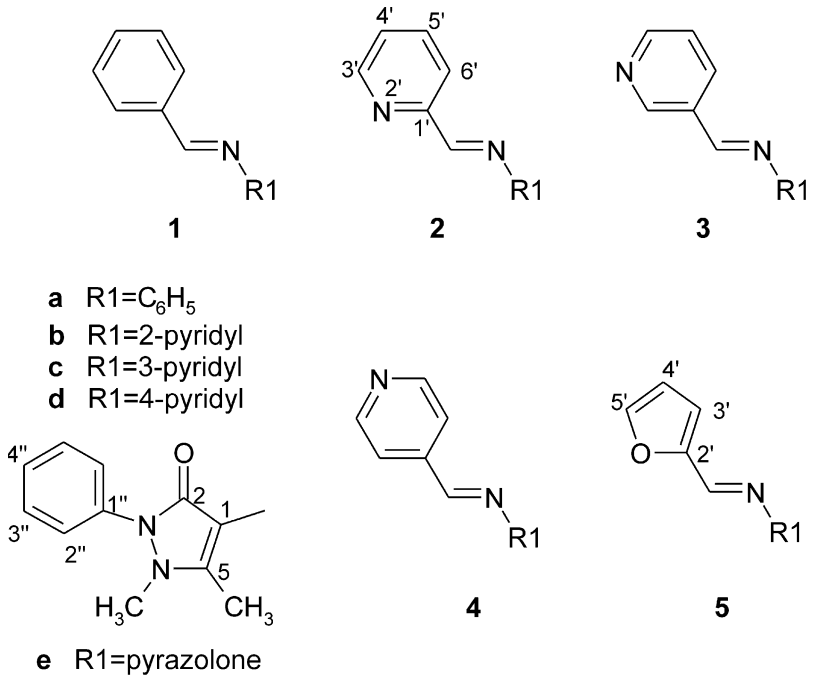


Scheme 1. Substituted aldimines (R1–N=CH–R2).

bond, 1,2-disubstitued by weak electrondonor and acceptor groups which allowed evaluation of substituent effects on ^{13}C and ^{15}N chemical shifts. As expected, substituent chemical shift (SCS) effects are larger in ^{15}N than in ^{13}C NMR. The present results showed that resonance stabilization [7] alone is not sufficient to secure a planar arrangement in these systems due to abnormally large torsion angles for the planes defined by the C=N and the aryl groups in both solid state, determined by X-ray [8], and solution, evidenced by NMR [9]. This distortion has been explained theoretically [10], and our results suggest that these systems can be stabilized by a stereoelectronic interaction.

2. Results

NMR spectral analysis was based on multinuclear experiments. Thus connectivity was established from heteronuclear and homonuclear correlation spectroscopy (COSY and HETCOR $^{13}C-^{1}H$). ^{1}H and ^{13}C spectral assignment was preformed by simulation [11]. The quaternary carbons were distinguished on the basis of their distinct relaxation time and they were confirmed by comparison within the same series. ^{15}N NMR spectra were recorded using the INEPT pulse sequence with and without proton decoupling and assignments were based on HMQC $^{1}H-^{15}N$ spectra. The ^{1}H, ^{13}C and ^{15}N NMR have additive substituent effects which are evident in the aldimine moiety; the signals for the aromatic substituents showed the characteristic chemical shifts.

SCS for the CH=N group were calculated from the differences between the heteroaromatic substituent with the corresponding phenyl derivative. These parameters were found to be additive and the reference compound for estimation was **1a**. The average error for $\delta^{1}H$ was <0.1 ppm, whilst for $\delta^{13}C$ was <0.5 ppm and for $\delta^{15}N$ was up to 2.4 ppm.

The configuration of the C=N double bond was elucidated based on the lone pair effect [12] and the observed $^{1}J_{CH}$ value. The stereochemistry around the carbon–nitrogen double bond was *E* for all compounds.

Contrary to previous reports [8] of **1a**, **2a**, **3a** and **4a**, X-ray diffraction of compounds **1e**, **2e**, **3e**, **4e** and

5e showed a planar arrangement of the aryl groups with the double bond C=N.

The compounds were also analyzed by ultraviolet and infrared spectroscopy.

3. Discussion

3.1. ^{13}C NMR

The ^{13}C NMR data for aldimines **1a** to **5e** are summarized in Table 1. The chemical shift range for the phenyl, pryridyl, pyrazolone or furanyl substituents is characteristic for each particular system and depends on whether it is attached to the carbon or nitrogen atom of the aldimine system. The imine carbon showed smaller SCS than the nitrogen, the furanyl group induced the largest effect (**5a**–**5e**) shifted to low frequency (145–150 ppm); the remaining substituents induced shifts to high frequency (<3 ppm). The resonance of iminic carbons containing a phenyl group experienced larger shift effects than those containing a pyridyl group. SCS were estimated by subtracting the chemical shifts for the molecule containing a heterocyclic substituent from the corresponding phenyl analogue. These effects were found to be additive (Table 2).

The one bond coupling constant, $^{1}J_{CH}$ (Table 1) showed a trend and its particular value is characteristic for the heterocycle. As previously noted for the chemical shifts, an aryl group has a stronger effect on the imine carbon than on nitrogen. The 2-pyridyl derivatives (**2a**–**2e**) exhibited the largest $^{1}J_{CH}$ value (164–170 Hz), followed by the 4-pyridyl derivatives **4a**–**4e** (162–169 Hz). A significant increment in $^{1}J_{CH}$ value was observed upon substitution by pyrazolone (**1e**, **2e**, **3e**, **4e** and **5e**) or 2-pyridyl groups (**1b**, **3b**, **4b**, **5b** and **2a**–**2e**) at the iminic nitrogen due to favorable electronic interaction and the absence of steric hindrance in these systems.

3.2. ^{15}NMR

^{15}N chemical shift effects were found to be larger than ^{13}C effects, except for furanyl derivatives, compounds **5a**–**5e**, which had the same SCS in both nuclei. ^{15}N NMR data are summarized in Table 3. Substitution at the imine nitrogen by a heterocycle has an electron-donor effect, as evidenced by the fact that the signals are shifted to lower frequency. ^{15}N chemical shift reveled that a heterocyclic group bonded to the imine carbon shifted the resonance to high frequency, except for the furanyl group, compounds **5a**–**5e**, which evidenced an electrodonation contribution. These effects were additive, as shown in table 2 the C-4-pyridyl derivatives (**4a** to **4e**) experienced the largest shift, followed by the C-2-pyridyl (**2a**–**2e**), and C-3-pyridyl (**3a**–**3e**), which showed almost the same magnitude effect as the *N*-3-pyridyl, but in opposite direction (compounds **1c**, **2c**, **3c**, **4c** and **5c**). The largest shift to higher frequency was observed in the pyrazolone derivatives (**1e**, **2e**, **3e**, **4e** and **5e**), followed by the furanyl group (**5a**–**5e**), and the *N*-2-pyridyl derivatives (**1b**, **2b**, **3b**, **4b** and **5b**) while no effect was observed upon introduction of a *N*-4-pyridyl moiety (**1d**, **2d**, **3d**, **4d** and **5d**). The ^{15}N substituent effects for the heterocyclic nitrogen ring were negligible, except for pyrazolone derivatives **1e**, **2e**, **3e**, **4e** and **5e**.

The value for the $^{2}J(^{15}N,^{1}H)$ of the imine nitrogen with the aldimine proton is in the range from 3.3 to 6.4 Hz, indicating that all imines had a *E* configuration [13]. The $^{2}J(^{15}N, ^{1}H)$ (Table 3) value with the nitrogen of the pyridyl group depended on the position of the substituent. 2-Substituted derivatives showed values 12 ± 1 Hz while 3- or 4-substitued showed two bond couplings of 22 ± 1 Hz, independently of their position.

3.3. ^{1}H NMR

The ^{1}H NMR spectra were resolved by simulation as second order coupling system. Analysis of $^{3}J_{HH}$ (Table 4) showed that the phenyl hydrogen had the largest observed value, whilst the furanyl group had the smallest. This value was relatively constant regardless of the position of the substituent. The long-range coupling constants (Table 4) also showed small substituent effects.

The proton chemical shifts (Table 5) evidenced the electron-donating character of the furanyl group since, the resonances were shifted to a lower frequency compared to those derivatives with a phenyl group. The aldimine hydrogen in the pyrazolone derivatives (**1e**, **2e**, **3e**, **4e** and **5e**) appeared at the highest frequency and this was attributed to low steric

Table 1
^{13}C NMR, chemical shifts and one bond $^{1}H-^{13}C$ coupling constants for aldimines **1–5**

Comp.	C=N	R1						R2					
		1	2	3	4	5	6	1′	2′	3′	4′	5′	6′
1a	160.5	152.2	121.3	129.2	126.4	129.2	121.3	136.4	128.9	128.8	131.5	128.8	128.9
	158.5		*158.8*	*160.2*	*161.2*	*160.2*	*158.8*		*161.1*	*161.0*	*161.3*	*161.0*	*161.1*
1b	162.9	161.1	–	148.9	121.9	138.1	119.8	135.9	129.5	128.8	131.9	128.8	129.5
	162.1			*178.7*	*165.0*	*160.1*	*165.0*		*161.1*	*159.1*	*161.1*	*159.1*	*161.1*
1c	162.2	147.9	142.7	–	147.3	123.8	129.0	135.8	129.1	129.0	132.1	129.0	129.1
	158.8		*179.6*		*179.6*	*164.0*	*163.0*		*159.9*	*162.0*	*160.9*	*162.0*	*159.9*
1d	163.5	159.4	116.2	150.0	–	150.0	116.2	134.9	128.8	128.5	131.9	128.5	128.8
	159.6		*163.7*	*177.1*		*177.1*	*163.7*		*159.3*	*161.4*	*160.9*	*161.4*	*159.3*
1e[a]	157.3	152.3	161	–	–	118.8	–	138.1	128.0	128.7	130.3	128.7	128.0
	166.3								*160.4*	*162.1*	*160.4*	*162.1*	*160.4*
2a	160.6	150.9	121.1	129.2	126.7	129.2	121.1	154.5	–	149.7	125.1	136.6	121.8
	163.7		*159.8*	*160.4*	*161.5*	*160.4*	*159.8*			*178.9*	*164.0*	*162.9*	*165.6*
2b	163.2	160.5	–	148.9	122.4	138.1	119.6	154.1	–	149.9	125.4	136.6	123.0
	165.9			*178.6*	*164.7*	*161.1*	*164.9*			*179.4*	*164.0*	*163.2*	*165.5*
2c	162.3	146.6	142.9	–	147.7	123.7	127.6	153.8	–	149.7	125.5	136.7	122.1
	164.0		*179.8*		*N.D.*	*165.6*	*166.8*			*179.6*	*163.3*	*163.1*	*N.D.*
2d	163.6	158.2	115.6	150.7	–	150.7	115.6	153.7	–	149.8	125.9	136.9	122.4
	163.7		*164.7*	*178.7*		*178.7*	*164.7*			*179.7*	*164.4*	*163.3*	*167.3*
2e[b]	156.7	152.8	160.6	–	–	118.1	–	156.6	–	150.0	124.3	136.6	121.6
	170.4									*178.4*	*163.4*	*161.7*	*163.9*
3a	156.9	151.1	120.7	129.0	126.3	129.0	120.7	131.5	150.6	–	151.7	123.5	134.6
	160.4		*160.1*	*160.6*	*161.5*	*160.6*	*160.1*		*178.9*		*179.4*	*164.2*	*164.1*
3b	159.5	159.9	–	148.6	122.1	137.9	119.9	131.1	151.2	–	152.1	123.5	135.1
	163.7			*178.4*	*164.2*	*161.9*	*163.6*		*179.4*		*179.4*	*164.7*	*164.6*
3c	159.0	147.0	142.4	–	147.4	123.8	127.7	131.2	150.8	–	152.2	123.7	135.1
	160.7		*179.3*		*180.1*	*165.1*	*163.6*		*180.4*		*180.1*	*164.8*	*164.5*
3d	159.9	158.0	115.2	150.5	–	150.5	115.2	130.6	150.8	–	152.4	123.6	134.9
	161.6		*164.4*	*177.5*		*177.5*	*164.4*		*178.7*		*180.2*	*165.1*	*164.7*
3e[c]	153.7	152.3	160.6	–	–	118.2	–	133.6	149.9	–	150.7	123.7	134.2
	167.6								*179.7*		*179.0*	*164.1*	*164.4*
4a	157.8	150.7	120.8	129.1	126.9	129.1	120.8	142.6	122.1	150.3	–	150.3	122.1
	162.3		*159.3*	*160.9*	*161.7*	*160.9*	*159.3*		*164.3*	*180.0*		*180.0*	*164.3*
4b	160.3	159.5	–	148.6	122.6	138.0	120.4	142.1	122.4	150.3	–	150.3	122.4
	165.4			*178.6*	*164.7*	*162.2*	*164.7*		*166.0*	*180.0*		*180.0*	*166.0*
4c	159.4	146.2	142.3	–	147.7	123.4	127.4	141.7	121.9	150.2	–	150.2	121.9
	162.3		*179.6*		*179.8*	*165.3*	*163.8*		*164.7*	*179.7*		*179.7*	*164.5*
4d	160.8	157.7	115.1	150.4	–	150.4	115.1	141.5	122.1	150.3	–	150.3	122.1
	163.5		*163.0*	*177.8*		*177.8*	*163.0*		*164.5*	*179.8*		*179.8*	*164.5*
4e[d]	153.9	152.6	160.4	–	–	117.8	–	144.9	121.5	150.3	–	150.3	121.5
	169.8								*162.1*	*178.6*		*178.6*	*162.1*
5a	147.8	151.4	121.0	129.2	126.3	129.2	121.0	–	152.1	116.4	112.3	145.7	–
	161.7		*159.6*	*160.4*	*161.4*	*160.4*	*159.6*			*176.7*	*177.7*	*204.0*	
5b	149.9	160.3	–	148.9	122.4	138.5	121.2	–	152.4	119.1	112.8	146.7	–
	165.4			*178.0*	*164.8*	*161.8*	*164.4*			*172.7*	*177.3*	*203.9*	
5c	148.9	146.9	142.6	–	147.0	123.4	127.5	–	151.4	117.5	112.3	146.1	–
	161.9		*179.6*		*179.6*	*165.0*	*163.0*			*175.4*	*177.5*	*204.5*	
5d	150.0	158.2	116.0	150.8	–	150.8	116.0	–	151.2	118.4	112.4	146.6	–
	162.4		*163.6*	*177.2*		*177.2*	*163.6*			*177.8*	*177.0*	*204.4*	
5e[e]	144.9	151.1	160.8	–	–	118.7	–	–	153.4	115.0	112.1	145.9	–
	169.2									*178.5*	*166.1*	*203.4*	

$^{1}J(^{13}C-^{1}H)$ in italics; N.D, not determinated; Compounds **1e–1d**, **2a**, **3a** and **4a** have been previously reported [9a].

[a] $\delta^{13}C$: N–CH_3 = 35.9, $^{1}J_{CH}$ = 140.5, C–CH_3 = 10.2, $^{1}J_{CH}$ = 129.9, N–C_6H_5: C_i = 135.0, C_o = 124.6, $^{1}J_{CH}$ = 163.4, C_m = 129.4, $^{1}J_{CH}$ = 162, C_p = 127.1, $^{1}J_{CH}$ = 162.3.

[b] $\delta^{13}C$: N–CH_3 = 35.9, $^{1}J_{CH}$ = 140.8, C–CH_3 = 10.6, $^{1}J_{CH}$ = 130.0, N–C_6H_5: C_i = 134.9, C_o = 125.1, $^{1}J_{CH}$ = 163.7, C_m = 129.6, $^{1}J_{CH}$ = 162.5, C_p = 127.5, $^{1}J_{CH}$ = 162.4.

[c] $\delta^{13}C$: N–CH_3 = 35.7, $^{1}J_{CH}$ = 140.8, C–CH_3 = 10.2, $^{1}J_{CH}$ = 130.2, N–C_6H_5: C_i = 134.6, C_o = 124.8, $^{1}J_{CH}$ = 163.7, C_m = 129.4, $^{1}J_{CH}$ = 162.6, C_p = 127.3, $^{1}J_{CH}$ = 161.9.

[d] $\delta^{13}C$: N–CH_3 = 35.6, $^{1}J_{CH}$ = 140.9, C–CH_3 = 10.2, $^{1}J_{CH}$ = 130.1, N–C_6H_5: C_i = 134.5, C_o = 125.0, $^{1}J_{CH}$ = 164.0, C_m = 129.5, $^{1}J_{CH}$ = 162.4, C_p = 127.6, $^{1}J_{CH}$ = 162.0.

[e] $\delta^{13}C$: N–CH_3 = 35.9, $^{1}J_{CH}$ = 140.6, C–CH_3 = 10.5, $^{1}J_{CH}$ = 129.8, N–C_6H_5: C_i = 134.8, C_o = 124.6, $^{1}J_{CH}$ = 163.3, C_m = 129.4, $^{1}J_{CH}$ = 162.3, C_p = 127.1, $^{1}J_{CH}$ = 162.4.

Table 2
^{1}H, ^{13}C and ^{15}N NMR substituent chemical shifts effects (SCS) for the aldimine group

N=C–H	$\Delta\delta^{1}H$		$\Delta\delta^{13}C$		$\Delta\delta^{15}N$	
	R1	**R2**	**R1**	**R2**	**R1**	**R2**
2-Pyridyl	0.74	0.14	2.4	0.0	−6.8	10.3
3-Pyridyl	0.04	0.08	1.6	−3.5	−7.8	6.6
4-Pyridyl	−0.04	0.03	2.8	−2.8	−3.8	14.6
Pyrazolone	1.31	–	−3.4	–	−25.6	–
Furanyl	–	−0.10	–	−13.0	–	−11.1

Reference compound: **1a**, $\delta^{1}H = 8.39$, $\delta^{13}C = 160.5$, $\delta^{15}N = -55.6$.

strain and through space interaction with the lone pair of the carbonyl group, as previously noted. A similar effect was observed in the *N*-2-pyridyl derivatives (**1b**, **2b**, **3b**, **4b** and **5b**). In these compounds the pyridine nitrogen was oriented on the same side as the aldimine hydrogen. The X-ray diffraction of the pyrazolone derivatives confirmed this arrangement.

3.4. X-ray diffraction

Adequate crystals for X-ray diffraction were obtained for compounds **1e**, **2e**, **3e**, **4e** and **5e** (Table 6): the torsion angle between the pyrazolone and the C=N double bond planes ranged from 1 to 7.5°; the corresponding values for the aryl group was 4.4–13° (Table 7). The bond between the pyrazolone and imine groups was *s-trans*, only the $N-CH_3$ and the $N-C_6H_5$ substituents of the pyrazolone moiety showed deviation from the main plane due to the steric effect (Fig. 1). The torsion angles obtained in the pyrazolone derivatives differed considerably from the results of the X-ray analysis [8] of compounds **1a**, **2a**, **3a** and **4a** which reported that the torsion angle between the aryl group and the imine bond was between 29 and 41°. This effect cannot be attributed to crystal packing because the same angles were determined by ^{13}C NMR in solution [9].

The distance from the aldimine hydrogen to the pyrazolone carbonyl was 2.32 ± 0.2 Å (Table 7) while that between the aldimine hydrogen or the imine nitrogen with the aryl group was less than 2.63 Å, except for the structure of the furanyl derivative **5e** which exhibited a larger distance (2.818 Å), due to the existence of a five member ring (Table 7). No intermolecular interactions were observed in the lattice (Fig. 2).

Contrary to a previous of X-ray diffraction report [8] of compounds **2a**, **3a** and **4a**, no disorder of the pyridine ring was observed. The X-ray structure of the 3-pyridine derivative **3e** showed that, in this case, the nitrogen of the aromatic group and the nitrogen of the imine group are *cis* (Fig. 3, Table 8). The 2-pyridine derivative **1e** had two rotamers in the unit cell, one with the nitrogen *syn* to the imine bond and the other one in an *anti* position (Fig. 4). The *syn*

Table 3
^{15}N NMR, chemical shift and two bond $^{1}H-^{15}N$ coupling constants for aldimines **1–5**

Compound	C=N		**R1**		**R2**	
	$\delta^{15}N$	$^{n}J_{NH}$	$\delta^{15}N$	$^{n}J_{NH}$	$\delta^{15}N$	$^{n}J_{NH}$
1a	−55.66	4.1	–	–	–	–
1b	−60.94	4.6	−93.98	11.7	–	–
1c	−61.79	4.8	−65.54	21.9	–	–
1d	−58.02	5.2	−78.42	20.9	–	–
1e	−79.97	3.7	−249.70[a]	4.8[b]	–	–
			−198.80[c]	5.9[d]		
2a	−43.70	6.4	–	–	−63.53	11.9
2b	−50.07	3.8	−91.88	11.5	−64.21	11.1
2c	−52.43	4.8	−65.77	21.1	−65.19	11.1
2d	−48.51	4.0	−76.46	20.7	−64.45	12.3
2e	−70.00	4.0	−247.60[a]	5.2[b]	−68.50	11.7
			−199.80[c]	6.1[d]		
3a	−46.92	3.7	–	–	−67.84	21.1
3b	−54.96	4.5	−93.70	12.0	−67.37	21.3
3c	−55.87	4.5	−66.43	21.5	−68.27	20.7
3d	−51.80	4.4	−76.04	21.6	−66.86	21.4
3e	−73.97	4.4	−248.07[a]	4.5[b]	−70.05	19.9
			−199.10[c]	5.3[d]		
4a	−38.80	5.4	–	–	−61.13	21.6
4b	−46.87	4.4	−93.14	12.2	−59.39	21.5
4c	−47.58	4.4	−64.95	21.6	−59.13	22.1
4d	−43.43	3.7	−75.89	21.1	−58.55	21.1
4e	−66.82	4.4	−246.90[a]	6.1[b]	−66.66	24.4
			−199.30[c]	6.6d[d]		
5a	−67.01	4.1	–	–	–	–
5b	−73.43	3.3	−95.62	13.7	–	–
5c	−73.23	3.7	−65.50	22.6	–	–
5d	−69.21	4.1	−77.54	20.9	–	–
5e	−89.21	3.7	−249.53[a]	4.8[b]	–	–
			−199.08[c]	5.9[d]		

[a] $N-CH_3$.
[b] $^{3}J(^{15}N-C-C-^{1}H)$; $N-CH_3$.
[c] $N-C_6H_5$.
[d] $^{3}J(^{15}N-N-C-^{1}H)$; $N-C_6H_5$.

Table 4
Three bond and long-range H–H coupling constants (Hz) in aldimines **1**–**5**

Comp.	HC=N-3	**R1**							**R2**						
		2–3	2–4	3–4	3–5	4–5	4–6	5–6	2′–3′	2′–4′	3′–4′	3′–5′	4′–5′	4′–6′	5′–6′
1a	0.3	8.0	1.2	7.4	1.8	7.4	1.2	8.0	7.9	1.6	7.4	1.3	7.4	1.6	7.9
1b	0.5	–	–	4.9	1.9	7.3	1.1	7.8	7.5	1.4	7.2	1.6	7.2	1.4	7.5
1c	0.4	–	0.3	–	–	4.8	1.5	8.1	7.7	1.4	7.4	1.5	7.4	1.4	7.7
1d	0.4	5.0	–	–	1.0	–	–	5.0	7.9	1.7	7.0	1.4	7.0	1.7	7.9
1e	0.4	–	–	–	–	–	–	–	7.9	1.7	7.5	1.7	7.5	1.7	7.9
2a	0.4	8.1	1.2	7.6	1.7	7.6	1.2	8.1	–	–	4.8	1.7	7.5	1.2	7.9
2b	0.3	–	–	4.8	2.0	7.5	1.1	7.8	–	–	4.8	1.7	7.6	1.2	7.9
2c	0.3	–	0.3	–	–	4.8	1.5	7.9	–	–	4.9	1.7	7.6	1.2	8.0
2d	0.3	5.0	–	–	1.4.	–	–	5.0	–	–	4.8	1.7	7.5	1.2	7.9
2e	0.3	–	–	–	–	–	–	–	–	–	4.8	1.7	7.6	1.2	7.9
3a	–	7.9	1.2	7.5	1.3	7.5	1.2	7.9	–	0.3	–	–	4.8	1.7	7.8
3b	–	–	–	4.9	2.0	7.3	1.1	7.9	–	0.3	–	–	4.8	1.7	7.8
3c	–	–	0.4	–	–	4.7	1.5	8.2	–	0.4	–	–	4.9	1.7	8.0
3d	–	5.3	–	–	–	–	–	5.3	–	0.3	–	–	4.9	1.7	8.0
3e	–	–	–	–	–	–	–	–	–	0.3	–	–	4.8	1.7	8.0
4a	0.4	7.4	1.3	7.5	1.7	7.5	1.3	7.4	5.0	–	–	0.4	–	–	5.0
4b	0.3	–	–	4.8	1.9	7.6	1.1	7.8	5.0	–	–	0.4	–	–	5.0
4c	0.5	–	0.4	–	–	4.8	1.5	8.2	4.9	–	–	0.4	–	–	4.9
4d	0.4	5.2	–	–	0.4	–	–	5.2	5.0	–	–	0.4	–	–	5.0
4e	0.4	–	–	–	–	–	–	–	5.0	–	–	0.4	–	–	5.0
5a	0.2	7.8	1.2	7.6	2.2	7.6	1.2	7.8	–	–	3.5	0.8	1.8	–	–
5b	0.3	–	–	4.8	1.7	7.5	1.1	7.9	–	–	3.5	0.8	1.8	–	–
5c	0.2	–	0.3	–	–	4.8	1.5	8.1	–	–	3.5	0.7	1.8	–	–
5d	0.2	5.2	–	–	0.4	–	–	5.2	–	–	3.5	0.7	1.8	–	–
5e	0.3	–	–	–	–	–	–	–	–	–	3.5	0.7	1.9	–	–

rotamer showed a distance of 2.794 Å between the aromatic nitrogen to the imine nitrogen.

3.5. UV and IR analyses

Analyses of the ultraviolet spectra of imine derivatives **1a**–**5e** showed that heterocyclic azines, such as the pyridyl group, were weak acceptors and furan acted as a π-donor. Compounds containing a N=C bond substituted by two pyridine groups showed an hypsochromic shift with respect to phenyl substituted ones. This effect was stronger in substances that had a phenyl group bonded to an imine carbon. The derivatives that had an α-furanyl group bonded to an iminic carbon showed a bathochromic shift.

The infrared spectra showed the characteristic stretching bands for the conjugated imine bond, all of which were in the same region, thus precluding unequivocal assignment.

4. Conclusions

For the first time, the complete NMR analyses of the ^{1}H, ^{13}C and ^{15}N chemical shift as well as the coupling constants for a series 25 di-aryl-aldimines, including the new derivatives **2c**, **3d**, **4b**, **4c** and **5c**, is reported.

The interaction between the lone pair of the pyrazolone carbonyl group or nitrogen of *N*-2-pyridine with the aldimine hydrogen was evidenced by an increase in the $^{1}J_{CH}$ value (3.2 ± 0.8 and 7.3 ± 0.4 Hz, respectively). In these compounds, the aldimine hydrogen is shifted to higher frequency, in the ^{1}H NMR spectra ($\Delta\delta^{1}H$ 1.3 and 0.7 respectively). The UV of these compounds showed a blue UV shift and a planar arrangement in the solid state, established by X-ray diffraction studies of aldimines **1e**, **2e**, **3e**, **4e** and **5e**. The distance between the aldimine hydrogen and the oxygen of the carbonyl group was shorter than the sum of the Van der Walls radii (2.32 ± 0.02 Å).

Table 5
^{1}H NMR, chemical shift (δ) for aldimines **1**–**5**

Comp.	HC=N	R1					R2				
		2	**3**	**4**	**5**	**6**	**2′**	**3′**	**4′**	**5′**	**6′**
1a	8.39	7.19	7.35	7.20	7.35	7.19	7.87	7.42	7.42	7.42	7.87
1b	9.14	–	8.47	7.12	7.69	7.31	7.98	7.44	7.46	7.44	7.98
1c	8.41	8.49	–	8.46	7.28	7.48	7.89	7.45	7.50	7.45	7.89
1d	8.31	6.98	8.54	–	8.53	6.98	7.87	7.44	7.48	7.44	7.87
1e[a]	9.76	–	–	–	–	–	7.86	7.41	7.39	7.41	7.86
2a	8.60	7.28	7.38	7.24	7.38	7.28	–	8.67	7.28	7.72	8.17
2b	9.22	–	8.52	7.19	7.79	7.38	–	8.75	7.36	7.75	8.20
2c	8.62	8.58	–	8.53	7.36	7.60	–	8.74	7.41	7.84	8.21
2d	8.52	7.08	8.61	–	8.61	7.08	–	8.74	7.43	7.85	8.18
2e[b]	9.78	–	–	–	–	–	–	8.64	7.23	7.70	8.03
3a	8.46	7.22	7.39	7.25	7.39	7.22	9.00	–	8.68	7.38	8.26
3b	9.22	–	8.50	7.19	7.75	7.35	9.10	–	8.71	7.40	8.33
3c	8.53	8.52	–	8.51	7.36	7.57	9.00	–	8.73	7.44	8.31
3d	8.45	7.05	8.60	–	8.60	7.05	9.03	–	8.85	7.45	8.29
3e[c]	9.78	–	–	–	–	–	9.01	–	8.60	7.34	8.17
4a	8.40	7.24	7.41	7.28	7.41	7.24	7.74	8.72	–	8.72	7.74
4b	9.15	–	8.49	7.19	7.74	7.36	7.79	8.75	–	8.75	7.79
4c	8.47	8.53	–	8.52	7.34	7.56	7.76	8.76	–	8.76	7.76
4d	8.40	7.06	8.60	–	8.60	7.06	7.76	8.78	–	8.78	7.76
4e[d]	9.71	–	–	–	–	–	7.69	8.66	–	8.66	7.69
5a	8.27	7.23	7.37	7.22	7.37	7.23	–	6.94	6.53	7.59	–
5b	9.11	–	8.46	7.16	7.74	7.41	–	7.06	6.57	7.65	–
5c	8.29	8.52	–	8.46	7.29	7.53	–	7.02	6.56	7.64	–
5d	8.23	7.06	8.57	–	8.57	7.06	–	7.06	6.59	7.66	–
5e[e]	9.63	–	–	–	–	–	–	6.78	6.50	7.56	–

[a] δ^1H : N–CH_3 = 3.15, C–CH_3 = 2.49, N–C_6H_5: H_o = 7.41, H_m = 7.48, H_p = 7.32.
[b] δ^1H : N–CH_3 = 3.13, C–CH_3 = 2.46, N–C_6H_5: H_o = 7.36, H_m = 7.44, H_p = 7.29.
[c] δ^1H : N–CH_3 = 3.19, C–CH_3 = 2.50, N–C_6H_5: H_o = 7.40, H_m = 7.49, H_p = 7.36.
[d] δ^1H : N–CH_3 = 3.22, C–CH_3 = 2.51, N–C_6H_5: H_o = 7.39, H_m = 7.50, H_p = 7.36.
[e] δ^1H : N–CH_3 = 3.15, C–CH_3 = 2.48, N–C_6H_5: H_o = 7.40, H_m = 7.48, H_p = 7.32.

These observations agree with previous reports [14] concerning hydrogen bond interactions.

The ^{15}N chemical shift showed additive substituent effects for the imine nitrogen and negligible effects in the heterocycle. Similar observations were derived from careful evaluation of the ^{13}C and ^{1}H data.

5. Experimental part

5.1. Instruments

^{1}H, ^{13}C and ^{15}N NMR spectra were recorded with a Bruker 300 Avance spectrometer equipped with a 5 mm multinuclear probe using $CDCl_3$ solution (0.9 mmol of the compound per 0.4 ml of solvent). Chemical shifts were referenced [15] to internal $(CH_3)_4Si$ ($\delta^1H = 0$, $\delta^{13}C$=0) and neat CH_3NO_2 (δ^{15}N for $\Xi^{15}N = 10.136767$ MHz). ^{1}H NMR spectra were recorded at 300 MHz. The ^{13}C NMR spectra were determined at 75.47 MHz with [16] and without [17] decoupling using the nuclear Overhauser enhancement method. ^{15}N NMR spectra were obtained at 30.38 MHz by INEPT methods [18] HMQC ^{1}H–^{15}N spectra were obtained on a Jeol Eclipse +400 spectrometer at 399.79 and 40.51 MHz respectively using the pulse field gradient sequence [19] with a 5 mm reverse detection multinuclear probe.

Melting points were measured on a Mel-Temp 3.0 (laboratory device inc. USA) and are given without correction. Elemental analyses were performed on

Table 6
Crystal data for compounds **1e**, **2e**, **3e**, **4e**, **5e**

	Compounds				
	1e	**2e**	**3e**	**4e**	**5e**
Empirical formula	$C_{18}H_{17}N_3O$	$C_{17}H_{16}N_4O$	$C_{17}H_{16}N_4O$	$C_{17}H_{16}N_4O$	$C_{16}H_{15}N_3O_2$
Formula weight	291.36	292.34	292.34	292.34	281.32
Crystal size (nm)	0.15 × 0.17 × 0.1	0.25 × 0.2 × 0.17	0.5 × 0.57 × 0.15	0.62 × 0.17 × 0.05	0.4 × 0.4 × 0.1
Crystal color	Yellow	Yellow	Yellow	Yellow	Orange
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/a$	$P2_1/a$	$P2_1/a$	$P2_1/c$
Unit cell dimensions (Å)	$a = 12.9980(3)$	$a = 13.8069(4)$	$a = 6.9907(2)$	$a = 7.0044(2)$	$a = 11.1637(1)$
	$b = 6.8704(2)$	$b = 10.0367(3)$	$b = 25.1699(6)$	$b = 24.9126(6)$	$b = 9.9139(1)$
	$c = 17.1969(1)$	$c = 23.1931(6)$	$c = 8.6300(2)$	$c = 8.6854(3)$	$c = 13.6443(1)$
	$\beta = 91.027(7)$	$\beta = 105.343(2)$	$\beta = 97.364(1)$	$\beta = 98.034(1)$	$\beta = 106.4050(5)$
Volume $(Å)^3$	1535.5(8)	3099.45(15)	1505.97(7)	1500.71(8)	1448.62(8)
Z	4	8	4	4	4
Density (calculated mg/m^3)	1.26	1.253	1.289	1.294	1.28
Absorption coefficient (cm^{-1})	0.75	0.82	0.84	0.84	0.82
$F(000)$	616	1232	616	616	592
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
θ range for collection(°)	2.16–20	3.40–26.36	3.40–27.45	3.41–27.88	2.23–25
Index range	$-12 \le h \le 12$	$-17 \le h \le 17$	$-9 \le h \le 9$	$-9 \le h \le 9$	$-12 \le h \le 13$
	$0 \le k \le 6$	$-12 \le k \le 12$	$-30 \le k \le 32$	$-32 \le k \le 9$	$-11 \le k \le 0$
	$0 \le l \le 16$	$-28 \le l \le 28$	$-11 \le l \le 11$	$-11 \le l \le 11$	$-16 \le l \le 0$
Reflections collected	1659	10691	6023	6042	2706
Independent reflection	1430	6280	3358	3517	2494
Observed reflection	488	3036	1887	1733	1679
CCDC	194856	194857	194858	194859	194855

CCDC, Cambridge Crystallographic Data Center. Radiation and wavelength: Mo Kα, $\lambda = 0.71073$.

a Thermo Finnigan Flash 1112. Mass spectra were obtained by electronic ionization at 70 eV in a Hewlett Packard HP-5989 spectrometer. UV spectra were recorded on a Perkin–Elmer lambda 12 using CH_2Cl_2 as solvent. Infrared spectra were determined in CH_2Cl_2 using a Perkin–Elmer 16F PC FT-IR spectrometer.

X-ray monocrystal diffraction analyses for compounds **1e** and **5e**, collection, structure resolution and refinement were performed using an

Table 7
Selected torsion angles, distances and angles

Torsion angle (°)	**1e**	**2e**		**3e**	**4e**	**5e**
C12–N3–C2–C3	−178.9	−172.5	175.5	179.9	179.7	177.9
R2–C12–N3	−174.9	−172.2	−174.8	−166.7	−171.1	−175.6
C3–C2–C1–O1	−177.9	176.7	174.8	−176.0	−175.9	−176.1
C5–N2–N1–C6	−58.9	45.5	50.4	−52.7	−50.7	−52.8
C3–C2–N2–N1	−10.0	6.6	5.3	−6.2	−5.1	−6.4
Contact distance (Å)						
H12–O1	2.466	2.310	2.320	2.355	2.310	2.289
Aryl-H–N3	2.632	2.555	–	2.550	2.574	–
Aryl-H–H12	2.443	–	2.369	2.417	2.399	2.818
Contact angle (°)						
C12–H12–O1	123.03	126.31	126.56	123.81	126.25	130.27
Aryl-H–N3	91.36	97.74	–	98.40	96.87	-

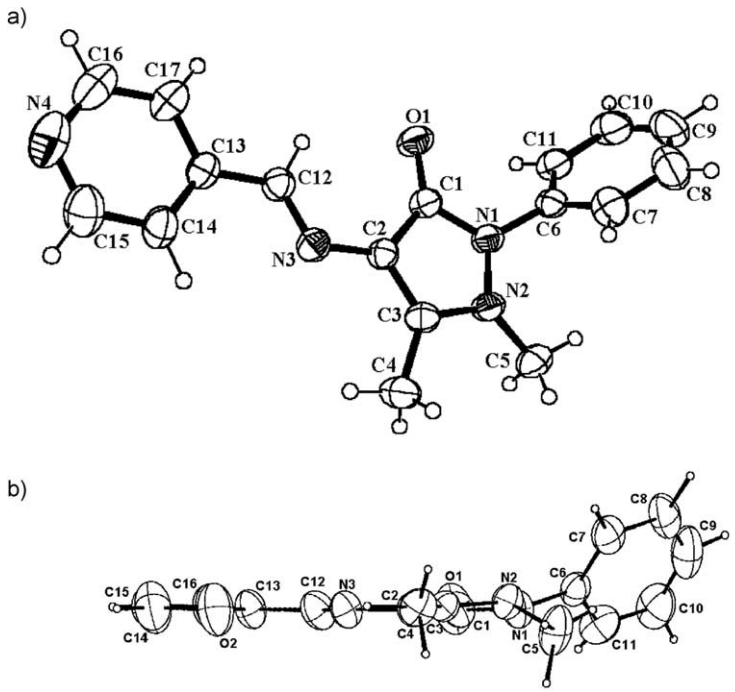


Fig. 1. X-ray molecular structure of aldimines (a) **4e** and (b) **5e**.

Enraf-Nonius CAD4 diffractometer. For compounds **2e**, **3e** and **4e**, the collection was preformed with a Siemens P4 instrument equipped with a CCD area detector. The WinGX software [20] was used for structure solution, refinement and data output. All hydrogen atoms in structures **2e**, **3e**, **4e** and **5e** were found in the difference Fourier map. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data as supplementary material. Copies of the data can be obtained free applying to: CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK; fax: +44-1223-336033 e-mail: deposit@ccdc.cam.ac.uk Cambridge registered numbers are: CCDC 194855 to 194859.

5.2. Reagents

Aldehydes and amines (Aldrich) were used as received except for aniline and furaldehyde that were distilled prior to use.

5.3. Preparation of compounds

The aldimines were prepared by the standard method, azeotropic distillation of the amine and the corresponding aldehyde in benzene (compounds **1a, 5a–5c**), toluene (compounds **1b**, **1c**, **2a–2d**, **3a–3d**, **4a–4d** and **5d**), *m*-xylene (compound **1d**) or methylenechloride (compounds **1e**, **2e**, **3e**, **4e**, **5e**) with *p*-toluenesulphonic acid as catalyst. The solvent was evaporated under vacuum. Imine–pyridine derivatives (**1b–1d**, **2b–2d**, **3b–3d**, **4b–4d** and **5b–5d**) were washed thoroughly with water. The pyrazolone derivatives **1e**, **2e**, **3e**, **4e** and **5e** were recrystallized from CH_2Cl_2/hexane and compounds **2c**, **3d**, **4c**, **5c** and **5d** were distilled under vacuum.

The spectral and physical properties of **1a** [21], **1b** [22], **1c** [23], **1d** [21], **1e** [24], **2a** [21], **2b** [25], **2e** [26], **3a** [21], **3b** [21], **3e** [25], **4a** [21], **4d** [27], **4e** [25], **5a** [28], **5b** [29] and **5e** [30] were in good agreement with previous reports.

N-(phenylmethylene)benzenamine, **1a**. m.p. 49–51 °C. EI-MS: *m/z*(%) 182(13)[$M^+ + 1$],

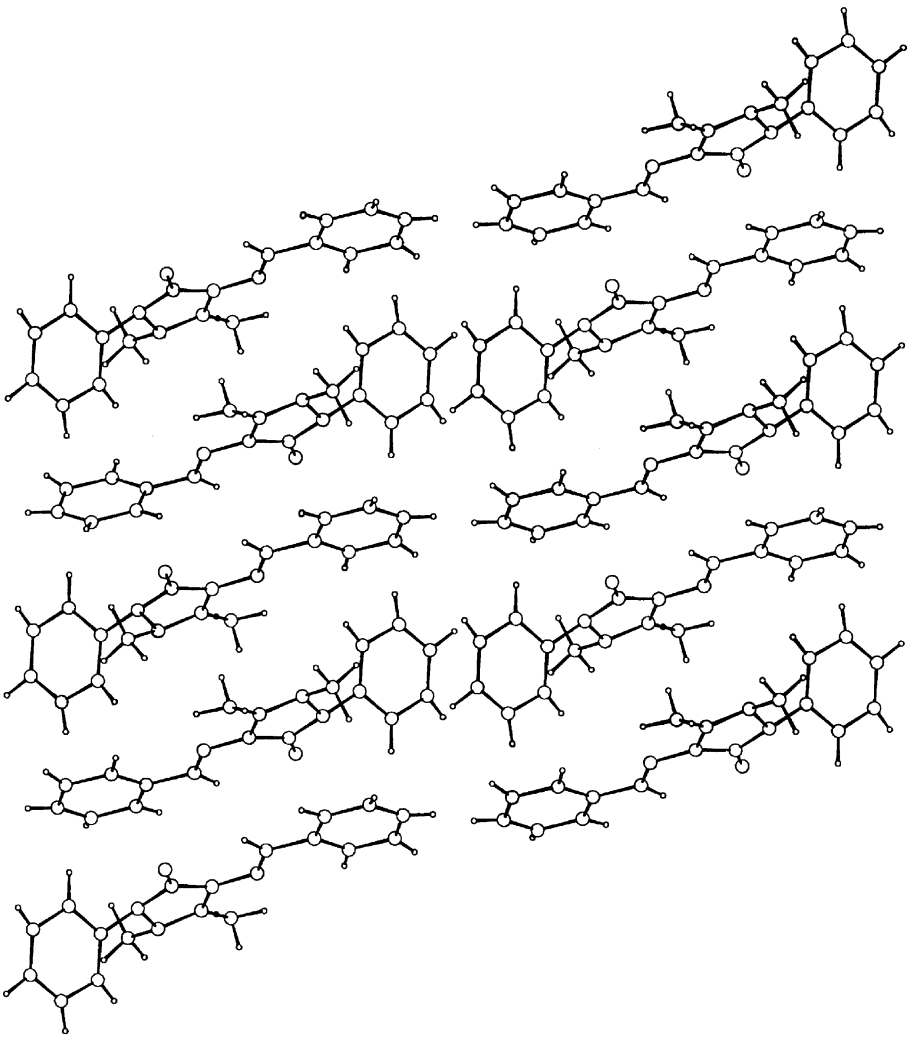


Fig. 2. Crystal packing for compound **1e**.

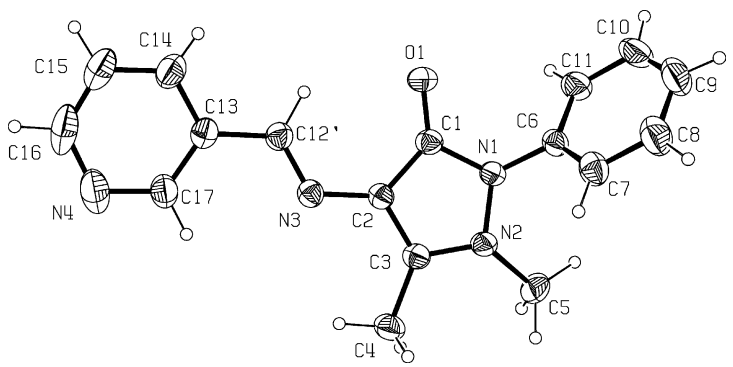
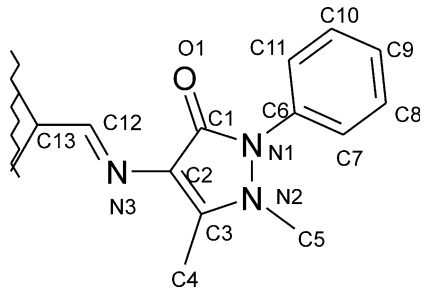


Fig. 3. X-ray diffraction for compound **3e**.

Table 8
Select bond distances and bond angles



	1a	2e		3e	4e	5e
Distances (Å)						
C13–C12	1.49(2)	1.468(4)	1.468(4)	1.464(3)	1.466(3)	1.425(4)
C12–N3	1.27(2)	1.276(3)	1.280(3)	1.279(2)	1.285(2)	1.283(3)
N3–C2	1.40(1)	1.395(3)	1.395(3)	1.392(2)	1.397(2)	1.390(3)
C2–C3	1.36(2)	1.369(3)	1.372(3)	1.369(2)	1.372(3)	1.372(3)
C2 C1	1.43(2)	1.435(4)	1.437(4)	1.432(2)	1.436(3)	1.435(4)
C1–O1	1.23(2)	1.231(3)	1.236(3)	1.235(2)	1.234(2)	1.236(3)
C3–N2	1.36(1)	1.362(3)	1.356(3)	1.353(2)	1.352(3)	1.357(3)
C3–C4	1.48(2)	1.483(4)	1.482(4)	1.485(3)	1.481(3)	1.483(4)
N2–C5	1.46(2)	1.451(3)	1.456(3)	1.460(3)	1.456(2)	1.456(4)
C1–N1	1.40(1)	1.388(3)	1.396(3)	1.404(2)	1.402(2)	1.392(3)
N1–N2	1.42(1)	1.400(3)	1.399(3)	1.4052(19)	1.403(2)	1.400(3)
N1–C6	1.45(1)	1.428(3)	1.430(3)	1.424(2)	1.424(3)	1.427(3)
C6–C7	1.34(2)	1.370(4)	1.380(4)	1.378(3)	1.379(3)	1.387(4)
C7–C8	1.42(2)	1.382(4)	1.382(4)	1.376(3)	1.387(4)	1.382(4)
C8–C9	1.33(2)	1.372(5)	1.366(5)	1.365(4)	1.372(5)	1.365(5)
C9–C10	1.33(2)	1.361(6)	1.378(5)	1.362(4)	1.377(5)	1.378(5)
C10–C11	1.42(2)	1.378(5)	1.381(4)	1.391(4)	1.374(4)	1.375(5)
C11–C6	1.39(2)	1.379(4)	1.373(4)	1.375(3)	1.377(3)	1.376(4)
Angles (°)						
C13–C12–N3	121.3(15)	120.6(3)	122.3(3)	120.90(18)	120.9(2)	122.0(3)
C12–N3–C2	120.5(12)	121.3(2)	120.0(2)	120.99(16)	120.43(18)	120.9(2)
N3–C2–C1	130.1(13)	129.3(2)	128.9(2)	129.17(15)	129.00(17)	129.3(2)
N3–C2–C3	121.2(12)	122.5(2)	123.0(2)	122.67(15)	122.58(18)	122.6(2)
O1–C1–C2	131.5(13)	131.5(3)	131.8(2)	132.12(17)	132.17(18)	131.3(3)
O1–C1–N1	123.9(13)	123.7(3)	123.1(2)	122.60(16)	122.97(18)	123.5(3)
C1–C2–C3	108.0(11)	108.2(2)	108.0(2)	107.99(15)	108.25(17)	107.9(2)
C2–C3–C4	127.9(14)	129.3(3)	128.6(2)	128.67(19)	129.0(2)	128.6(2)
C2–C3–N2	111.4(13)	109.7(2)	109.9(2)	110.20(15)	109.87(17)	109.8(2)
C4–C3–N2	120.7(15)	121.0(3)	121.5(2)	121.12(17)	121.07(19)	121.6(2)
C3–N2–C5	126.1(13)	124.9(2)	125.0(2)	126.37(17)	126.91(17)	123.1(2)
C3–N2–N1	105.0(12)	106.9(2)	107.55(19)	107.50(13)	107.67(15)	107.4(2)
N1–N2–C5	117.6(12)	118.6(2)	118.3(2)	118.79(17)	119.40(16)	118.0(2)
C1–N1–N2	109.7(10)	109.7(2)	109.2(2)	108.59(13)	108.95(15)	109.1(2)
C1–N1–C6	120.8(11)	125.1(2)	124.5(2)	122.99(14)	122.03(16)	125.2(2)
N2–N1–C6	117.8(11)	121.0(2)	120.5(2)	119.41(14)	119.96(16)	119.8(2)
N1–C6–C7	122.9(13)	121.8(3)	120.7(3)	120.80(17)	120.77(19)	120.9(3)
N1–C6–C11	115.4(12)	117.8(3)	118.5(2)	118.51(19)	118.3(2)	118.4(3)
C6–C7–C8	118.3(17)	119.3(4)	119.0(3)	119.5(2)	118.9(3)	118.7(3)
C7–C8–C9	120.7(18)	120.7(4)	120.5(3)	120.3(3)	120.6(3)	120.9(4)
C8–C9–C10	121.3(19)	119.5(4)	120.3(3)	120.3(3)	119.8(3)	119.9(3)
C9–C10–C11	120.7(18)	120.8(4)	119.8(4)	120.5(3)	120.5(3)	120.3(4)
C10–C11–C6	117.4(16)	119.3(4)	119.6(3)	118.8(3)	119.5(3)	119.5(4)
C11–C6–C7	121.7(14)	120.4(3)	120.8(3)	120.7(2)	120.9(2)	120.6(3)

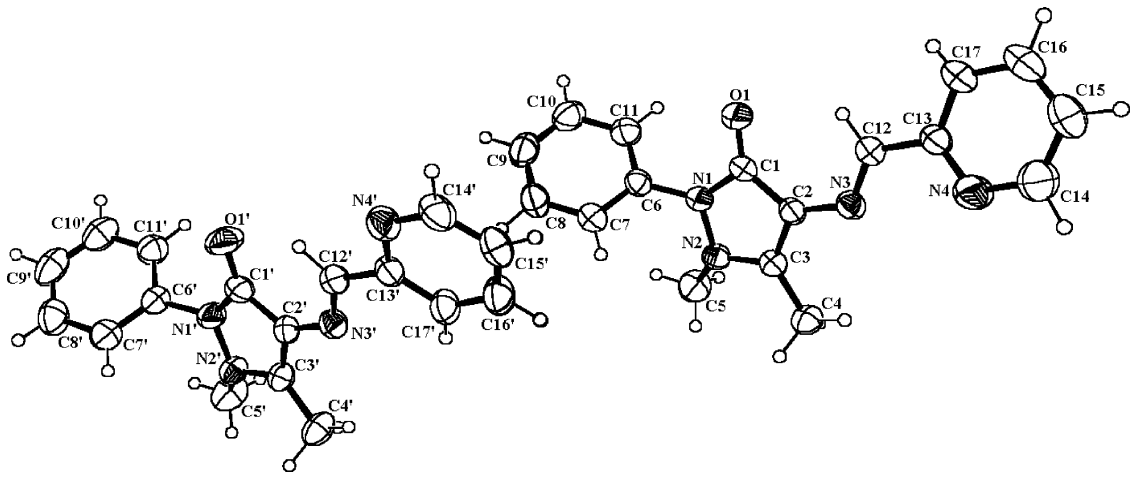


Fig. 4. X-ray molecular structure of compound **2e**, showing two independent molecules in the unit cell.

181(94)[M^+], 180(100), 104(12), 77(61), 51(31). IR ν_{max} (cm^{-1}): 1694, 1628, 1592, 1580. UV λ_{max}/nm (ε) 263 (16537), 235 (10647), 307 (7929).

N-(phenylmethylene)-2-pyridinamine, **1b**. m.p. 102–106 °C. EI-MS: *m/z*(%) 183(1)[$M^+ + 1$], 182(11)[M^+], 181(27), 79(100), 52(28), 51(30). IR ν_{max} (cm^{-1}): 3020, 1704, 1676, 1622, 1586, 1562. UV λ_{max}/nm (ε) 251 (11662), 298 (10387).

N-(phenylmethylene)-3-pyridinamine, **1c**. EI-MS: *m/z*(%) 183(13)[$M^+ + 1$], 182(100)[M^+], 181(99), 105(8), 89(16), 78(73), 51(42). IR ν_{max} (cm^{-1}): 3050, 1628, 1578. UV λ_{max}/nm (ε) 271 (14057), 259 (13276).

N-(phenylmethylene)-4-pyridinamine, **1d**. EI-MS: *m/z*(%) 183(14)[$M^+ + 1$], 182(100)[M^+], 181(85), 105(7), 89(9), 78(75), 51(63). IR ν_{max} (cm^{-1}): 1706, 1630, 1598, 1584. UV λ_{max}/nm (ε) 263 (12553).

N-(phenylmethylene)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one, **1e**. m.p. 175–177 °C. EI-MS: *m/z*(%) 292(8)[$M^+ + 1$], 291(37)[M^+], 199(10), 188(11), 121(17), 77(13), 56(100), 28(10). IR ν_{max} (cm^{-1}): 3048, 1704, 1654, 1584. UV λ_{max}/nm (ϵ) 335 (5982), 241 (5050), 259 (4817).

N-(2-pyridinemethylene)benzenamine, **2a**. EI-MS: *m/z*(%) 183(7)[$M^+ + 1$], 182(52)[M^+], 181(100), 155(28), 154(29), 79(22), 77(43), 51(36). IR ν_{max} (cm^{-1}): 1630, 1592, 1568, 1498,1486, 1468, 1436 1266. UV λ_{max}/nm (ε) 236 (6977), 282 (4478), 318 (4134).

N-(2-pyridinemethylene)-2-pyridinamine, **2b**. EI-MS: *m/z*(%) 184(9)[$M^+ + 1$], 183(48)[M^+], 182(100), 156(33), 155(27), 105(25), 79(90), 78(64), 52(42), 51(46). IR ν_{max} (cm^{-1}): 1626, 1592, 1570, 1472, 1438, 1364, 1270(t). UV λ_{max}/nm (ε) 247 (5862), 289 (4342).

N-(2-pyridinemethylene)-3-pyridinamina, **2c**. b.p. 105–108 °C/0.003 mmHg. Yield 85%. Anal. Calcd. for $C_{11}H_9N_3$: C = 72.11%, H = 4.95%, N = 22.93%. Found: C = 71.92, H = 5.04, N = 23.11. EI-MS: *m/z*(%) 184(6)[$M^+ + 1$], 183(23)[M^+], 182(100), 155(19), 78(21), 51(24). IR ν_{max} (cm^{-1}): 1630, 1588, 1570, 1474, 1438, 1416, 1272(d). UV λ_{max}/nm (ε) 248 (15115), 282 (13232).

N-(2-pyridinemethylene)-4-pyridinamina, **2d**. EI-MS: *m/z*(%) 184(5)[$M^+ + 1$], 183(40)[M^+], 182(100), 155(18), 79(97), 78(37), 52(34), 51(42). IR ν_{max} (cm^{-1}): 1636, 1270, 910. UV λ_{max}/nm (ε) 248 (6805).

N-(2-pyridinemethylene)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one, **2e**. m.p. 161–165 °C. EI-MS: *m/z*(%) 293(6)[$M^+ + 1$], 292(27)[M^+], 200(21), 172(24), 121(18), 77(11), 56(100). IR ν_{max} (cm^{-1}): 1658, 1594, 1566, 1498, 1468, 1456, 1424,1412, 1270(d). UV λ_{max}/nm (ε) 343 (18710), 258 (16371), 246 (15202).

N-(3-pyridinemethylene)benzenamine, **3a**. EI-MS: *m/z*(%) 183(16)[$M^+ + 1$], 182(100)[M^+], 181(77), 104(13), 77(53), 51(33). IR ν_{max} (cm^{-1}): 1706, 1628,

1590, 1572, 1486, 1452, 1420 1266(d). UV λ_{max}/nm (ε) 238 (5597), 245 (4556), 320 (2777).

N-(3-pyridinemethylene)-2-pyridinamine, **3b**. m.p. 64–68 °C. Yield 64%. Anal. Calcd. for $C_{11}H_9N_3$: C = 72.11%, H = 4.95%, N = 22.93%. Found: C = 72.24, H = 5.17, N = 22.90. EI-MS: *m/z*(%) 184(3)[$M^+ + 1$], 183(17)[M^+], 182(100), 155(13), 105(6), 79(46), 78(23), 52(23), 51(26). IR ν_{max} (cm^{-1}): 1624, 1588, 1562, 1462, 1434, 1266(d). UV λ_{max}/nm (ε) 240 (15153), 270 (6297), 290 (6101).

N-(3-pyridinemethylene)-3-pyridinamine, **3c**. m.p. 20–25 °C. Yield 73%. Anal. Calcd. for $C_{11}H_9N_3$: C = 72.11%, H = 4.95%, N = 22.93%. Found: C = 72.11, H = 5.23, N = 22.76. EI-MS: *m/z*(%) 184(16)[$M^+ + 1$], 183(100)[M^+], 182(54), 105(12), 78(40), 51(24). IR ν_{max} (cm^{-1}): 1706, 1630, 1590, 1572, 1476, 1420 1264(d). UV λ_{max}/nm (ε) 246 (10626), 278 (10626).

N-(3-pyridinemethylene)-4-pyridinamine, **3d**. b.p. 74–77 °C/0.007 mmHg. m.p. 20–25 °C. Yield 53%. Anal. Calcd. for $C_{11}H_9N_3$: C = 72.11%, H = 4.95%, N = 22.93%. Found: C = 72.39, H = 5.21, N = 23.13. EI-MS: *m/z*(%) 184(23)[$M^+ + 1$], 183(100)[M^+], 182(59), 105(12), 78(32), 51(33). IR ν_{max} (cm^{-1}): 1634, 1586, 1574, 1558, 1506, 1488, 1422 1268(d). UV λ_{max}/nm (ε) 250 (14886), 272 (11832).

N-(3-pyridinemethylene)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one, **3e**. m.p. 201 to 205 °C. EI-MS: *m/z*(%) 293(7)[$M^+ + 1$], 292(29)[M^+], 200(9), 188(13), 121(25), 77(15), 56(100). IR ν_{max} (cm^{-1}): 1654, 1594, 1498, 1456, 1410 1266(d). UV λ_{max}/nm (ε) 341 (15226), 254 (14081).

N-(4-pyridinemethylene)benzenamine, **4a**. EI-MS: *m/z*(%) 183(15)[$M^+ + 1$], 182(100)[M^+], 181(46), 104(30), 77(60), 51(37). IR ν_{max} (cm^{-1}): 1628, 1598, 1558, 1486, 1452, 1410 1268 (d). UV λ_{max}/nm (ε) 231 (3796), 257 (2603), 322 (1616).

N-(4-pyridinemethylene)-2-pyridinamine, **4b**. m.p. 40–44 °C. Yield 73%. Anal. Calcd. for $C_{11}H_9N_3$: C = 72.11%, H = 4.95%, N = 22.93%. Found: C = 71.92, H = 5.07, N = 22.65. EI-MS: *m/z*(%) 184(8)[$M^+ + 1$], 183(41)[M^+], 182(100), 155(17), 79(87), 78(35), 52(30), 51(41). IR ν_{max} (cm^{-1}): 1624, 1598, 1564, 1554, 1462, 1434, 1412 1270 (d). UV λ_{max}/nm (ε) 234 (10289), 241 (9747), 294 (4513).

N-(4-pyridinemethylene)-3-pyridinamine, **4c**. b.p. 105–108 °C/0.003 mmHg, m.p. 48–52 °C. Yield 93%. Anal. Calcd. for $C_{11}H_9N_3$: C = 72.11%, H = 4.95%, N = 22.93%. Found: C = 72.11, H = 4.96, N = 22.58. EI-MS: *m/z*(%) 184(17)[$M^+ + 1$], 183(100)[M^+], 182(43), 105(24), 79(25), 78(50), 51(32). IR ν_{max} (cm^{-1}): 1714, 1630, 1598, 1560, 1476, 1416 1268 (d). UV λ_{max}/nm (ε) 234 (12611), 273 (9399).

N-(4-pyridinemethylene)-4-pyridinamine, **4d**. m.p. 77–78.8 °C. EI-MS: *m/z*(%) 184(16)[$M^+ + 1$], 183(100)[M^+], 182(38), 105(25), 78(46), 51(48). IR ν_{max} (cm^{-1}): 1636, 1598, 1566, 1506, 1486, 1458, 1414 1270 (d). UV λ_{max}/nm (ε) 244 (11909).

N-(4-pyridinemethylene)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one, **4e**. m.p. 236.9–239 °C. EI-MS: *m/z*(%) 293(8)[$M^+ + 1$], 292(41)[M^+], 200(13), 188(19), 121(39), 77(14), 56(100). IR ν_{max} (cm^{-1}): 1660, 1572, 1498, 1414 1268 (d). UV λ_{max}/nm (ε) 349 (5962), 241 (5193), 255 (5193).

N-(2-furanylmethylene)-benzenamine, **5a**. m.p. 57–59 °C. EI-MS: *m/z*(%) 172(13)[$M^+ + 1$], 171(100)[M^+], 170(62), 142(30), 115(27), 77(65), 51(42), 38(24). IR ν_{max} (cm^{-1}): 3052, 1634, 1590, 1476. UV (CH_2Cl_2) λ_{max}/nm (ε) 286 (17365), 316 (12718), 229 (8560), 237 (6603).

N-(2-furanylmethylene)-2-pyridinamine, **5b**. EI-MS: *m/z*(%) 173(5)[$M^+ + 1$], 172(37)[M^+], 171(22), 144(48), 118(100), 79(76), 52(56), 51(54), 39(35). IR ν_{max} (cm^{-1}): 3026, 1696, 1624, 1614, 1594, 1584. UV λ_{max}/nm (ε) 282 (18946), 320 (17793), 247(11479).

N-(2-furanylmethylene)-3-pyridinamine, **5c**. b.p. 113–117 °C/0.01 mmHg. Yield 93%. Anal. Calcd. for $C_{10}H_8N_2O$: C = 69.79%, H = 4.68%, N = 16.27% O = 9.29%. Found: C = 69.48, H = 4.69, N = 16.43. EI-MS: *m/z*(%) 173(12)[$M^+ + 1$], 172(100)[M^+], 171(29), 118(30), 78(44), 52(27), 51(46), 39(28). IR ν_{max} (cm^{-1}): 3050, 1676, 1634, 1630, 1570, 1470, 1416. UV λ_{max}/nm (ε) 304 (10801), 232 (3240).

N-(2-furanylmethylene)-4-pyridinamine, **5d**. b.p. 84–87 °C/0.003 mmHg. m.p. 76.5 ⊣ 78.1 °C Anal. Calcd. for $C_{10}H_8N_2O$: C = 69.79%, H = 4.68%, N = 16.27% O = 9.29%. Found: C = 69.48, H = 4.69, N = 16.43. EI-MS: *m/z*(%) 173(11)[$M^+ + 1$], 172(100)[M^+], 171(31), 143(44), 78(46), 51(66), 39(34). IR ν_{max} (cm^{-1}): 3038, 1696, 1680, 1624. UV λ_{max}/nm (ε) 293 (18571).

N-(2-furanylmethylene)-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-one, **5e**. EI-MS: *m/z*(%) 282(6)[$M^+ + 1$], 281(33)[M^+], 172(10), 121(8),

77(8), 56(100), 51(11), 28(9). IR ν_{max} (cm^{-1}): 3054, 1656, 1596, 1552. UV λ_{max}/nm (ε) 339 (18664), 257 (9467).

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