Crystal structure of 1-(4-propanoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-oneimine) 2-aminobenzene, $C_{19}H_{20}N_4O$, and of 1-(4-butanoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-oneimine) 2-aminobenzene, $C_{20}H_{22}N_4O$

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Abstract

$C_{19}H_{20}N_4O$, monoclinic, $P12_1/n1$ (No. 14), $a = 9.228(1)$ Å, $b = 9.3599(8)$ Å, $c = 19.781(3)$ Å, $\beta = 100.69(2)°$, $V = 1678.9$ Å^3, $Z = 4$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.123$, $T = 293$ K.

$C_{20}H_{22}N_4O$, triclinic, $P\bar{1}$ (No. 2), $a = 8.830(2)$ Å, $b = 9.171(2)$ Å, $c = 11.400(3)$ Å, $\alpha = 77.96(2)°$, $\beta = 77.41(2)°$, $\gamma = 83.97(2)°$, $V = 879.4$ Å^3, $Z = 2$, $R_{gt}(F) = 0.042$, $wR_{ref}(F^2) = 0.119$, $T = 293$ K.

Source of material

The compounds $C_{19}H_{20}N_4O$ (**1**) and $C_{20}H_{22}N_4O$ (**2**) were synthesized and purified adopting a method reported elsewhere [1] in the 1,2-diaminobenzene to 3H-pyrazol-3-one mole ratio of 1:1. The pink ethanolic solution obtained was left overnight at room temperature and the orange deposits that came out were filtered and recrystallized from ethanol to obtain brown crystals of **1** and **2.**

Experimental details

The hydrogen atoms H1, H2 and H3 of both compounds were located in difference Fourier maps and refined freely isotropically, all other were included in the refinement in calculated positions riding on their carrier atoms.

Discussion

Schiff bases have been studied extensively [2, 3] for possible application in the synthesis of stable transition metal complexes that are biologically active [4]. Application of these bases as potential extraction and spectrophotometric reagents and as important stereochemical models in transition metal coordination chemistry have equally received various attention [1, 2, 3, 5]. Reports have also appeared indicating that some types of Schiff bases can behave in solution as bidentate or as tridentate ligands or can coordinate in both ways depending upon the nature of metal ion or the type of substituent [6, 7].

As part of our ongoing investigation on the condensation reaction between amines and 4-acyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-one units the title compounds were synthesised and characterized by X-ray diffraction studies to confirm the coupling of the two units in the 1:1 ratio. The ORTEP plots of **1** and **2** show that both compounds contain intramolecular hydrogen bonds of the type =C—N—H···O=C formed between the imine and pyrazolone units of the compounds. The bond distances of the hydrogen bonds are 1.741(43) Å (**1**) and 1.758(43) Å (**2**). In both compounds, the hydrogen bond formation is associated with slight molecular distortion of the aminobenzene unit from coplanarity with the pyrazole ring unit. In **1** the dihedral angle between the plane of the aminobezene unit and that of the pyrazole ring unit is 61.0° whereas in **2** it is 60.90°. However, the hydrogen bond formation ensured that the imine unit is nearly coplanar with the pyrazole ring, with the N3–C11–C3–C4 torsion angle adopting values of –2.30° and –3.26° for **1** and **2** respectively. Hence, in both compounds the pyrazole ring and the =C—NH imine substituent are virtually coplanar with atoms N1, N2, N3, O1, C1–C4 and C11 lying within the least-squares plane of the pyrazole and =C—N—H···O=C chelate ring systems. The presence of the =C–NH group in the compounds has an important role to play in the coordination chemistry of these compounds with transition metal ions. In **1** the phenyl group is twisted away from a plane defined by the pyrazole ring with an angle of 2.61° while in (**2**) the same twist occurred by 7.63°. Almost all 4-acyl substituted pyrazolones adopt this energetically more favourable orientation between the phenyl ring and the pyrazole ring in the final configuration of the asymmetric ligand. We are currently exploring the coordination chemistry of these ligands with transition metal ions.

1. 1-(4-Propanoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-oneimine) 2-aminobenzene, $C_{19}H_{20}N_4O$

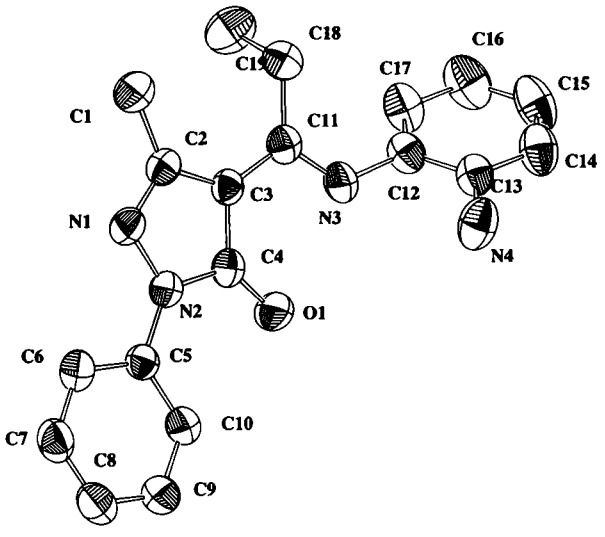

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Table 1. Data collection and handling.

Crystal:	light brown flat prism, size 0.04 × 0.22 × 0.50 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.81 cm^{-1}
Diffractometer, scan mode:	CAD4 (NONIUS), ω/2θ
$2\theta_{max}$:	39.98°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	1614, 1557
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1215
$N(param)_{refined}$:	226
Programs:	SHELXS-97 [8], SHELXL-97 [9]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1A)	4*e*	–0.0383	0.6868	0.3885	0.092
H(1B)	4*e*	0.0821	0.7541	0.3518	0.092
H(1C)	4*e*	–0.0577	0.843	0.3597	0.092
H(6)	4*e*	0.0303	0.6093	0.5992	0.059
H(7)	4*e*	0.0056	0.5410	0.7078	0.069
H(8)	4*e*	0.1094	0.6745	0.8024	0.070
H(9)	4*e*	0.2385	0.8794	0.7868	0.064
H(10)	4*e*	0.2646	0.9498	0.6789	0.058
H(14)	4*e*	0.3380	1.6384	0.4404	0.077
H(15)	4*e*	0.4957	1.6267	0.3643	0.090
H(16)	4*e*	0.5716	1.4086	0.3293	0.091
H(17)	4*e*	0.4875	1.2023	0.3716	0.078
H(18A)	4*e*	0.2029	1.1538	0.3303	0.062
H(18B)	4*e*	0.0926	1.0272	0.3324	0.062
H(19A)	4*e*	0.2708	0.9601	0.2679	0.114
H(19B)	4*e*	0.2859	0.8623	0.3332	0.114
H(19C)	4*e*	0.3966	0.9887	0.3315	0.114
H(1)	4*e*	0.316(5)	1.159(4)	0.510(2)	0.114
H(2)	4*e*	0.178(4)	1.517(4)	0.502(2)	0.092
H(3)	4*e*	0.157(4)	1.359(4)	0.503(2)	0.092

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	4*e*	0.0741(3)	0.7607(3)	0.5037(1)	0.049(2)	0.043(2)	0.048(2)	–0.006(1)	0.004(1)	–0.006(2)
N(2)	4*e*	0.1549(2)	0.8347(2)	0.5599(1)	0.048(2)	0.038(2)	0.044(2)	–0.005(1)	0.007(1)	–0.001(1)
N(3)	4*e*	0.3027(3)	1.1696(3)	0.4573(1)	0.059(2)	0.040(2)	0.056(2)	–0.008(1)	0.013(2)	0.007(2)
N(4)	4*e*	0.2165(3)	1.4331(3)	0.4979(2)	0.064(2)	0.055(2)	0.091(2)	–0.012(2)	0.027(2)	–0.013(2)
O(1)	4*e*	0.2985(2)	1.0419(2)	0.5769(1)	0.068(2)	0.052(1)	0.049(1)	–0.022(1)	0.005(1)	–0.004(1)
C(1)	4*e*	0.0123(4)	0.7733(3)	0.3811(2)	0.068(2)	0.057(2)	0.056(2)	–0.011(2)	0.002(2)	–0.007(2)
C(2)	4*e*	0.0915(3)	0.8295(3)	0.4485(2)	0.043(2)	0.041(2)	0.045(2)	0.001(2)	0.009(2)	–0.005(2)
C(3)	4*e*	0.1823(3)	0.9525(3)	0.4648(2)	0.039(2)	0.035(2)	0.043(2)	0.004(2)	0.006(2)	–0.001(2)
C(4)	4*e*	0.2213(3)	0.9540(3)	0.5385(2)	0.042(2)	0.037(2)	0.050(2)	–0.004(2)	0.009(2)	–0.001(2)
C(5)	4*e*	0.1469(3)	0.7895(3)	0.6272(2)	0.042(2)	0.039(2)	0.041(2)	0.005(2)	0.009(2)	0.001(2)
C(6)	4*e*	0.0714(3)	0.6648(3)	0.6369(2)	0.052(2)	0.041(2)	0.057(2)	–0.001(2)	0.013(2)	–0.003(2)
C(7)	4*e*	0.0576(4)	0.6238(4)	0.7019(2)	0.069(2)	0.045(2)	0.062(3)	–0.001(2)	0.026(2)	0.006(2)
C(8)	4*e*	0.1193(4)	0.7029(4)	0.7585(2)	0.067(2)	0.055(2)	0.058(2)	0.013(2)	0.021(2)	0.013(2)
C(9)	4*e*	0.1962(3)	0.8251(4)	0.7489(2)	0.059(2)	0.051(2)	0.049(2)	0.006(2)	0.006(2)	0.003(2)
C(10)	4*e*	0.2111(3)	0.8678(3)	0.6844(2)	0.054(2)	0.043(2)	0.048(2)	–0.003(2)	0.009(2)	0.004(2)
C(11)	4*e*	0.2268(3)	1.0612(3)	0.4244(2)	0.039(2)	0.041(2)	0.050(2)	0.007(2)	0.013(2)	0.000(2)
C(12)	4*e*	0.3550(3)	1.2956(3)	0.4290(2)	0.041(2)	0.049(2)	0.057(2)	–0.006(2)	0.008(2)	0.007(2)
C(13)	4*e*	0.3087(3)	1.4267(3)	0.4506(2)	0.038(2)	0.046(2)	0.059(2)	–0.007(2)	0.006(2)	0.002(2)
C(14)	4*e*	0.3656(4)	1.5496(4)	0.4259(2)	0.049(2)	0.051(2)	0.090(3)	–0.001(2)	0.007(2)	0.008(2)
C(15)	4*e*	0.4611(4)	1.5428(4)	0.3809(2)	0.058(2)	0.062(3)	0.106(3)	–0.005(2)	0.019(2)	0.030(2)
C(16)	4*e*	0.5065(4)	1.4130(5)	0.3600(2)	0.061(2)	0.077(3)	0.096(3)	0.000(2)	0.034(2)	0.023(3)
C(17)	4*e*	0.4550(4)	1.2904(4)	0.3847(2)	0.063(2)	0.054(2)	0.080(2)	0.004(2)	0.021(2)	0.013(2)
C(18)	4*e*	0.1938(3)	1.0579(3)	0.3477(2)	0.049(2)	0.055(2)	0.050(2)	0.001(2)	0.010(2)	0.004(2)
C(19)	4*e*	0.2963(4)	0.9579(4)	0.3172(2)	0.077(3)	0.088(3)	0.072(2)	0.008(2)	0.033(2)	–0.016(2)

2. 1-(4-Butanoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-oneimine) 2-aminobenzene, $C_{20}H_{22}N_4O$

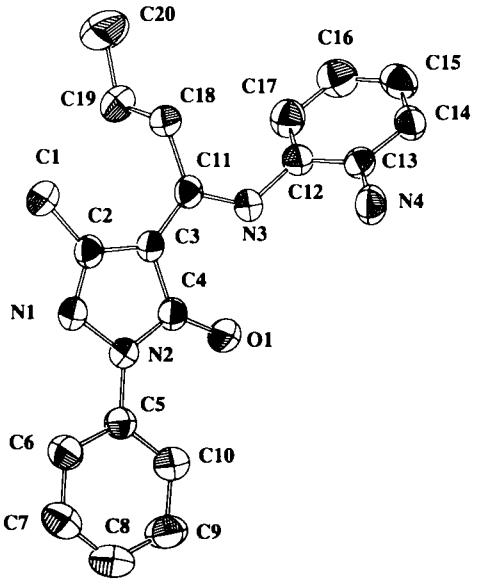

Table 4. Data collection and handling.

Crystal:	light brown prism, size 0.11 × 0.22 × 0.58 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.81 cm^{-1}
Diffractometer, scan mode:	CAD4 (NONIUS), ω/2θ
$2\theta_{max}$:	44°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2313, 2149
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1822
$N(param)_{refined}$:	239
Programs:	SHELXS-97 [8], SHELXL-97 [9]

Table 5. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1A)	2*i*	0.0625	0.1834	0.7574	0.086
H(1B)	2*i*	–0.0765	0.0972	0.7464	0.086
H(1C)	2*i*	–0.0664	0.2676	0.6887	0.086
H(6)	2*i*	0.0468	0.4306	0.3119	0.064
H(7)	2*i*	0.0645	0.5607	0.1143	0.079
H(8)	2*i*	0.2056	0.4596	–0.0482	0.086
H(9)	2*i*	0.3297	0.2268	–0.0105	0.081
H(10)	2*i*	0.3118	0.0926	0.1857	0.065
H(14)	2*i*	0.3509	–0.7213	0.6234	0.060
H(15)	2*i*	0.5188	–0.7548	0.7550	0.070
H(16)	2*i*	0.5882	–0.5533	0.8189	0.076

Table 5. Continued.

Atom	Site	*x*	*y*	*z*	U_{iso}
H(17)	2*i*	0.4963	–0.3167	0.7423	0.068
H(18A)	2*i*	0.1899	–0.2572	0.8104	0.055
H(18B)	2*i*	0.0756	–0.1142	0.8031	0.055
H(19A)	2*i*	0.3953	–0.0956	0.7968	0.071
H(19B)	2*i*	0.2664	0.0341	0.8130	0.071
H(20A)	2*i*	0.3316	–0.0706	1.0002	0.168
H(20B)	2*i*	0.2866	–0.2274	0.9895	0.168
H(20C)	2*i*	0.1577	–0.0979	1.0057	0.168
H(1)	2*i*	0.329(5)	–0.198(5)	0.495(4)	0.168
H(2)	2*i*	0.185(3)	–0.557(3)	0.505(2)	0.074(8)
H(3)	2*i*	0.159(3)	–0.389(3)	0.509(2)	0.068(7)

Table 6. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
N(1)	2*i*	0.0752(2)	0.2322(2)	0.4872(2)	0.053(1)	0.0404(9)	0.045(1)	–0.0020(7)	–0.0061(8)	–0.0138(8)
N(2)	2*i*	0.1683(2)	0.1696(2)	0.3916(1)	0.050(1)	0.0385(9)	0.0378(9)	–0.0021(7)	–0.0053(7)	–0.0086(7)
N(3)	2*i*	0.3078(2)	–0.2308(2)	0.5870(2)	0.060(1)	0.0363(9)	0.045(1)	–0.0013(8)	–0.0079(8)	–0.0097(8)
N(4)	2*i*	0.2158(2)	–0.4768(3)	0.5242(2)	0.070(1)	0.046(1)	0.065(1)	–0.000(1)	–0.023(1)	–0.019(1)
O(1)	2*i*	0.3219(2)	–0.0495(2)	0.3703(1)	0.074(1)	0.0503(9)	0.0447(9)	0.0104(7)	–0.0008(7)	–0.0125(7)
C(1)	2*i*	–0.0072(3)	0.1745(2)	0.7057(2)	0.070(1)	0.054(1)	0.046(1)	0.003(1)	–0.003(1)	–0.018(1)
C(2)	2*i*	0.0843(2)	0.1360(2)	0.5883(2)	0.047(1)	0.038(1)	0.045(1)	–0.0081(9)	–0.0068(9)	–0.012(1)
C(3)	2*i*	0.1826(2)	0.0072(2)	0.5658(2)	0.047(1)	0.035(1)	0.039(1)	–0.0053(9)	–0.0066(9)	–0.0110(9)
C(4)	2*i*	0.2347(2)	0.0323(2)	0.4348(2)	0.047(1)	0.038(1)	0.044(1)	–0.0042(9)	–0.0056(9)	–0.0119(9)
C(5)	2*i*	0.1786(2)	0.2486(2)	0.2698(2)	0.044(1)	0.043(1)	0.042(1)	–0.0100(9)	–0.0100(9)	–0.0064(9)
C(6)	2*i*	0.1042(2)	0.3886(2)	0.2471(2)	0.058(1)	0.049(1)	0.052(1)	–0.003(1)	–0.013(1)	–0.006(1)
C(7)	2*i*	0.1149(3)	0.4663(3)	0.1287(2)	0.073(2)	0.055(1)	0.065(2)	–0.001(1)	–0.021(1)	0.003(1)
C(8)	2*i*	0.1988(3)	0.4067(3)	0.0317(2)	0.082(2)	0.075(2)	0.050(1)	–0.007(1)	–0.017(1)	0.007(1)
C(9)	2*i*	0.2720(3)	0.2679(3)	0.0546(2)	0.074(2)	0.076(2)	0.044(1)	–0.001(1)	–0.005(1)	–0.005(1)
C(10)	2*i*	0.2623(2)	0.1875(2)	0.1721(2)	0.058(1)	0.055(1)	0.047(1)	–0.004(1)	–0.008(1)	–0.008(1)
C(11)	2*i*	0.2241(2)	–0.1249(2)	0.6413(2)	0.043(1)	0.038(1)	0.044(1)	–0.0104(9)	–0.0057(9)	–0.0123(9)
C(12)	2*i*	0.3614(2)	–0.3764(2)	0.6412(2)	0.048(1)	0.041(1)	0.041(1)	–0.0027(9)	–0.0032(9)	–0.0068(9)
C(13)	2*i*	0.3151(2)	–0.4977(2)	0.6040(2)	0.043(1)	0.043(1)	0.039(1)	–0.0027(9)	0.0021(9)	–0.0099(9)
C(14)	2*i*	0.3780(2)	–0.6388(2)	0.6480(2)	0.053(1)	0.040(1)	0.052(1)	–0.0019(9)	0.001(1)	–0.009(1)
C(15)	2*i*	0.4789(2)	–0.6591(2)	0.7267(2)	0.056(1)	0.051(1)	0.058(1)	0.007(1)	–0.001(1)	–0.002(1)
C(16)	2*i*	0.5215(3)	–0.5392(3)	0.7640(2)	0.057(1)	0.069(2)	0.062(2)	0.006(1)	–0.019(1)	–0.009(1)
C(17)	2*i*	0.4648(2)	–0.3985(2)	0.7195(2)	0.058(1)	0.055(1)	0.059(1)	–0.003(1)	–0.015(1)	–0.016(1)
C(18)	2*i*	0.1825(2)	–0.1507(2)	0.7781(2)	0.051(1)	0.044(1)	0.041(1)	–0.0053(9)	–0.0042(9)	–0.0082(9)
C(19)	2*i*	0.2876(3)	–0.0732(3)	0.8331(2)	0.073(2)	0.061(1)	0.050(1)	–0.004(1)	–0.017(1)	–0.019(1)
C(20)	2*i*	0.2637(5)	–0.1216(4)	0.9694(3)	0.180(4)	0.111(2)	0.059(2)	–0.032(2)	–0.041(2)	–0.018(2)

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