

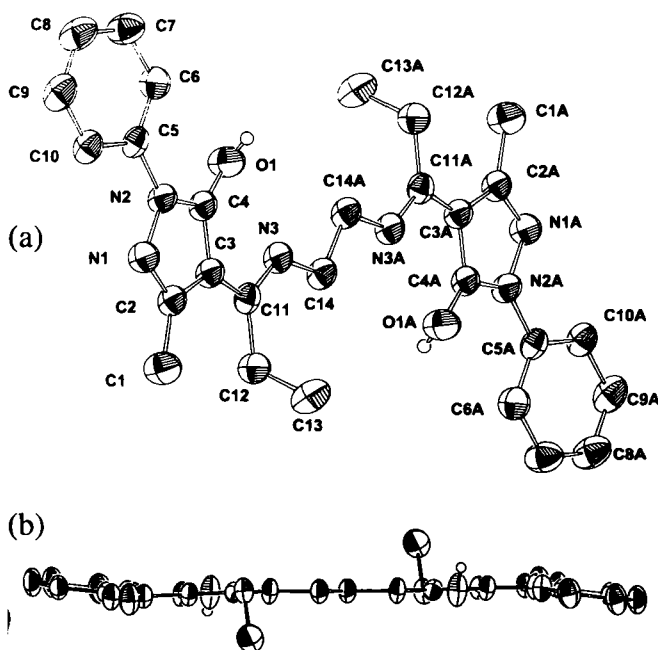
## Crystal structure of *N,N'*-ethylenbis(4-propanoyl-2,4-dihydro-5-methyl-2-phenyl-3*H*-pyrazol-3-oneimine), $C_{28}H_{32}N_6O_2$

B. A. Uzoukwu<sup>I</sup>, K. Gloe<sup>\*I</sup>, H. Duddeck<sup>II</sup> and O. Rademacher<sup>I</sup>

<sup>I</sup> Technische Universität Dresden, Institut für Anorganische Chemie, Mommsenstr. 13, D-01062 Dresden, Germany

<sup>II</sup> Universität Hannover, Institut für Organische Chemie, Schneiderberg 1B, D-30167 Hannover, Germany

Received September 1, 2000, CCDC-No. 1267/522



### Abstract

$C_{28}H_{32}N_6O_2$ , triclinic,  $P\bar{1}$  (No. 2),  $a = 7.911(3)$  Å,  $b = 8.250(3)$  Å,  $c = 9.978(3)$  Å,  $\alpha = 88.99(2)^\circ$ ,  $\beta = 86.60(2)^\circ$ ,  $\gamma = 75.91(2)^\circ$ ,  $V = 630.5$  Å<sup>3</sup>,  $Z = 1$ ,  $R_g(F) = 0.047$ ,  $wR_{ref}(F^2) = 0.144$ ,  $T = 293$  K.

### Source of material

The compound was synthesized and purified as reported elsewhere [1] in the amine to 3*H*-pyrazol-3-one mole ratio of 1:2. The pink ethanolic solution obtained was left overnight at room temperature and the white deposit that came out was filtered and recrystallized from ethanol to obtain crystals of the compound.

### Discussion

Schiff bases have been extensively studied and new designs of this class of imine ligands have appeared in the literature [1–5] for quite some time. This has been attributed to their 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 [3, 5]. 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 compound was synthesised and characterized by x-ray diffraction studies to confirm the coupling of the two units in the 1:2 ratio.

Figure (a) shows that the crystallographic center of inversion at the C14—C14A bond and the two pyrazoloneimine units are parallel to each other. The plot also shows that there are little or no intraligand interactions between the C4—O—H and N3=C11 groups in the molecule. Probably, this may be due to the long N...H distance of 3.170 Å recorded and the fact that the two O—H groups are actually *trans* to each other with respect to the planar pyrazoloneimine groups. The *anti* orientation of the two H ends of the O—H groups has been attributed to the slight displacement of the hydrogen atoms out of the plane defined by the pyrazole ring. The presence of the O—H groups in the ligand is of immense importance in coordination chemistry of transition metal complexes of imine ligands and the ability of the ligand to form stable complexes with metal ions [1]. Another plot of the molecule viewed from the side is presented in figure (b) and shows the two phenyl groups parallel to each other but twisted away from their respective pyrazole rings with a dihedral angle of 8.72°. The plot revealed the centrosymmetric nature of the ligand and the near coplanarity of the pyrazole ring with the imine substituent with the C4—C3—C11—N3 torsion angle adopting a value of 2.83°. Their tendency towards planarity has been attributed to an effective conjugation between the C11=N3 double bond of the imine and the C3=C4 double bond of the pyrazole ring. It also revealed the *trans* orientations of the two propanoyl substituents with respect to the plane of the pyrazoloneimine units. The bond lengths are typical of a compound of this type. The bond lengths of the C4=O1 and C11=N3 double bonds are 1.245(2) Å and 1.323(2) Å, respectively. The C14—C14A bond that is situated at the centrosymmetric point in the molecule has the longest C—C single bond length of 1.505(4) Å. Most of the bond angles are close to 120°. The atom centers that have deviated from ideal positions of trigonal geometry in the molecule are C2, C3 and C4. The deviation around C3 is due to the repulsion between C1 methyl and C12—C13 ethyl groups, resulting in the increase of C11—C3—C2 and C3—C2—C1 bond angles to 133.4(2)° and 130.5(2)°, respectively, and the decrease of N1—C2—C1 bond angle to 117.69(19)°. The resultant strain on the 5 membered pyrazole ring from repulsion along the C1—C2—C3 bond axis due to the activities stated above is the squeezing of the bond angle of C4—C3—C2 from a theoretical angle of 108° to 104.95(18)°. This happens to be the least bond angle recorded in the molecule. The O1—C4—C3 bond angle of 128.55(19)° that is virtually the same with the theoretical angle of 126° has been attributed to the absence of steric demands due to the displacement of the hydrogen atom out of the basal plane between O1 and N3 atoms.

\* Correspondence author  
(e-mail: karsten.gloe@chemie.tu-dresden.de)

**Table 1.** Data collection and handling.

Crystal:	white needle, size 0.07 × 0.14 × 0.58 mm
Wavelength:	Mo K <sub>α</sub> radiation (0.71073 Å)
μ:	0.83 cm <sup>-1</sup>
Diffractometer, scan mode:	CAD4 (Nonius), ω/2θ
2θ <sub>max</sub> :	48°
<i>N</i> ( <i>hkl</i> ) <sub>measured</sub> , <i>N</i> ( <i>hkl</i> ) <sub>unique</sub> :	2137, 1973
Criterion for <i>I</i> <sub>obs</sub> , <i>N</i> ( <i>hkl</i> ) <sub>gt</sub> :	<i>I</i> <sub>obs</sub> > 2 σ( <i>I</i> <sub>obs</sub> ), 1591
<i>N</i> ( <i>param</i> ) <sub>refined</sub> :	166
Programs:	SHELXS-97 [6], SHELXL-97 [7]

**Table 2.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>
H(1)	2i	0.3626	0.2914	0.8733	0.085
H(1A)	2i	0.5479	-0.2413	0.5176	0.084
H(1B)	2i	0.6680	-0.3477	0.6229	0.084
H(1C)	2i	0.7463	-0.2414	0.5153	0.084
H(6)	2i	0.5490	0.3960	0.8977	0.055
H(7)	2i	0.7100	0.5862	0.9407	0.066
H(8)	2i	0.9856	0.5565	0.8419	0.070
H(9)	2i	1.1008	0.3380	0.6992	0.065
H(10)	2i	0.9425	0.1468	0.6529	0.053
H(12A)	2i	0.2357	-0.3265	0.8245	0.052
H(12B)	2i	0.4037	-0.3464	0.7286	0.052
H(13A)	2i	0.1738	-0.3537	0.5989	0.090
H(13B)	2i	0.2295	-0.1873	0.5642	0.090
H(13C)	2i	0.0636	-0.1838	0.6591	0.090
H(14A)	2i	0.0721	-0.1747	0.9937	0.048
H(14B)	2i	-0.0317	-0.0704	0.8783	0.048

**Table 3.** Atomic coordinates and displacement parameters (in Å<sup>2</sup>).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>11</sub>	<i>U</i> <sub>22</sub>	<i>U</i> <sub>33</sub>	<i>U</i> <sub>12</sub>	<i>U</i> <sub>13</sub>	<i>U</i> <sub>23</sub>
O(1)	2i	0.3939(2)	0.1962(2)	0.9031(2)	0.0419(9)	0.062(1)	0.070(1)	-0.0235(8)	0.0220(8)	-0.0253(9)
N(1)	2i	0.7082(2)	-0.0004(2)	0.6599(2)	0.034(1)	0.053(1)	0.045(1)	-0.0136(8)	0.0109(8)	-0.0104(8)
N(2)	2i	0.6370(2)	0.1268(2)	0.7518(2)	0.0288(9)	0.049(1)	0.044(1)	-0.0162(8)	0.0072(7)	-0.0094(8)
N(3)	2i	0.2041(2)	-0.0262(2)	0.8955(2)	0.0277(9)	0.053(1)	0.045(1)	-0.0149(8)	0.0098(8)	-0.0078(8)
C(1)	2i	0.6450(3)	-0.2457(3)	0.5720(3)	0.049(1)	0.065(2)	0.056(1)	-0.021(1)	0.019(1)	-0.019(1)
C(2)	2i	0.6032(3)	-0.1012(3)	0.6649(2)	0.031(1)	0.050(1)	0.039(1)	-0.0140(9)	0.0057(9)	-0.0043(9)
C(3)	2i	0.4595(3)	-0.0466(3)	0.7607(2)	0.029(1)	0.046(1)	0.038(1)	-0.0126(9)	0.0057(9)	-0.0051(9)
C(4)	2i	0.4853(3)	0.1039(3)	0.8153(2)	0.025(1)	0.050(1)	0.041(1)	-0.0125(9)	0.0072(9)	-0.009(1)
C(5)	2i	0.7300(3)	0.2498(3)	0.7738(2)	0.030(1)	0.049(1)	0.038(1)	-0.0161(9)	-0.0026(9)	0.0022(9)
C(6)	2i	0.6607(3)	0.3829(3)	0.8579(2)	0.035(1)	0.051(1)	0.054(1)	-0.016(1)	0.009(1)	-0.004(1)
C(7)	2i	0.7570(3)	0.4970(3)	0.8832(3)	0.057(2)	0.056(1)	0.059(2)	-0.027(1)	0.008(1)	-0.009(1)
C(8)	2i	0.9210(3)	0.4797(3)	0.8242(3)	0.055(2)	0.071(2)	0.060(2)	-0.039(1)	0.009(1)	-0.008(1)
C(9)	2i	0.9894(3)	0.3494(3)	0.7393(2)	0.039(1)	0.077(2)	0.053(1)	-0.030(1)	0.008(1)	-0.002(1)
C(10)	2i	0.8955(3)	0.2342(3)	0.7121(2)	0.034(1)	0.059(1)	0.041(1)	-0.018(1)	0.0044(9)	-0.002(1)
C(11)	2i	0.3181(3)	-0.1123(3)	0.8049(2)	0.029(1)	0.046(1)	0.036(1)	-0.0096(9)	0.0003(9)	-0.0007(9)
C(12)	2i	0.2910(3)	-0.2726(3)	0.7534(2)	0.039(1)	0.046(1)	0.046(1)	-0.016(1)	0.008(1)	-0.004(1)
C(13)	2i	0.1792(4)	-0.2470(3)	0.6328(2)	0.066(2)	0.072(2)	0.052(1)	-0.033(1)	-0.005(1)	-0.008(1)
C(14)	2i	0.0447(3)	-0.0662(3)	0.9501(2)	0.031(1)	0.050(1)	0.043(1)	-0.0176(9)	0.0053(9)	-0.0013(9)

**Acknowledgment.** The authors wish to thank Alexander von Humboldt-Stiftung for Research Fellowship to B.A.U.

## References

- Uzoukwu, B. A.; Gloe, K.; Duddeck, H.: *N,N'*-Ethylenebis(1-phenyl-3-methyl-4-acylpyrazoloneimine) derivatives: Synthesis and UV, IR, <sup>1</sup>H and <sup>13</sup>C NMR spectral studies. *Indian J. Chem.* **37B** (1998) 1180-1183.
- Rao, S. N.; Mishra, D. D.; Maurya, R. C.; Rao, N. N.: Novel 8-coordinate *cis*-MoO<sub>2</sub>(VI) complexes with some 4-aminoantipyrene Schiff base derivatives. *Bull. Chem. Soc. Jap.* **68** (1995) 1589-1592.
- Rao, S. N.; Jaiswal, M. N.; Mishra, D. D.; Maurya, R. C.; Rao, N. N.: Synthesis and characterisation of *cis*-dioxomolybdenum(VI) Schiff base complexes derived from 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone. *Polyhedron* **12** (1993) 2045-2050.
- Topich, J.; Lyon J. T.: Synthesis and electrochemistry of *cis*-dioxomolybdenum(VI) complexes with tridentate Schiff base ligands containing O, N and S donor atoms. *Polyhedron* **3** (1984) 55-60.
- Uzoukwu, B. A.; Gloe, K.; Duddeck, H.: 4-Acylpyrazoloneimine Schiff bases and their metal complexes: Synthesis and spectroscopic studies. *Synth. React. Inorg. Met.-Org. Chem.* **28** (1998) 819-831.
- Sheldrick, G. M.: SHELXS-97. Program for the Solution of Crystal Structures. University of Göttingen, Germany 1997.
- Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1997.