Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

4,4′-Methylenediantipyrine monohydrate

Klaus Merz

Anorganische Chemie 1, Ruhr-Universität Bochum, Universitätsstrasse 150, D-41801 Bochum, Germany

Correspondence e-mail: klaus@merz.as

Received 11 February 2002
Accepted 19 February 2002
Online 28 February 2002

Key indicators

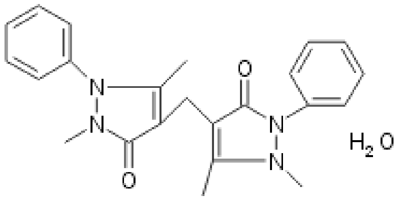
Single-crystal X-ray study
T = 203 K
Mean σ(C–C) = 0.003 Å
R factor = 0.047
wR factor = 0.130
Data-to-parameter ratio = 13.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

In the crystal structure of the title compound, $C_{23}H_{24}N_4O_2\cdot H_2O$, the 4,4′-methylenediantipyrine molecules are linked *via* hydrogen bonds through water molecules to form centrosymmetric dimers.

Comment

4,4′-Methylenediantipyrine reacts with titanium(IV) in a strongly acid medium to form a complex having an absorption maximum at around 285 nm (Minin, 1955). This reaction has been widely used for selective photometric determination of titanium(IV). We report here the structure and hydrogen-bonding behavior of the title compound, (I). 4,4-Methylenediantipyrine crystallized from acetone as the monohydrate in the space group $P2_1/c$. The molecular structure is shown in Fig. 1.



(I)

The structure is dominated by the angle of the bridging C atom, C8—C12—C13, between the two pyrazolone moieties. There is no conjugation between the pyrazolone moieties and the phenyl rings. In the molecule, the two phenyl rings and the two pyrazolone rings are oriented at 55.6 (1) and 54.0 (1)° with respect to each other. However, the N2—C1 and N4—C18 bonds are slightly shorter than the accepted N—C single-bond distance of 1.47 (1) Å (Allen *et al.*, 1987). This is in good agreement with the determined structures of antipyrine (Singh & Vijayan, 1973) and other metal–pyrazolone complexes (Vijayan & Viswamitra, 1968). All bond lengths lie between the corresponding single- and double-bond distances. In Allen *et al.* (1987), CH_3—C═C has a mean value of 1.503 Å, in good agreement with the value in this paper, *viz*. 1.491 Å. This might be partly due to the sp^2 hybridization state of atom C9. Distances and angles of special interest are given in Table 1.

Another striking feature of this compound is the orientation of the two pyrazolone rings. The differences between the molecular dimensions of free 4,4′-methylenediantipyrine monohydrate determined from the present study and the structure observed in the titanium(IV)–antipyrine complexes (Yuchi *et al.*, 1991) are significant. As a consequence of the

DOI: 10.1107/S1600536802003331

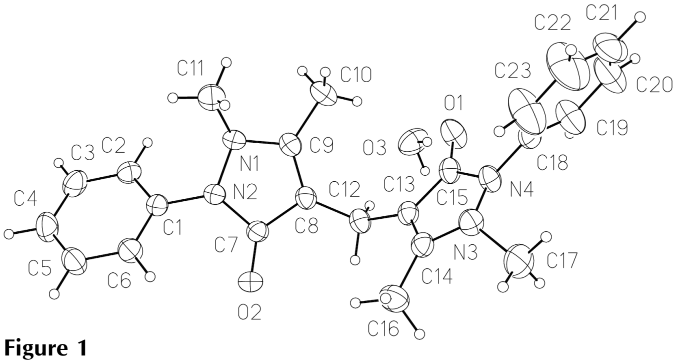


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids.

conformation of the bridging atom C12, the carbonyl groups of the pyrazolone moieties in 4,4′-methylenediantipyrine monohydrate are antiparallel. In contrast, 4,4′-methylenediantipyrine acts as a bidentate ligand to form eight-membered chelate rings with tin(IV) tetrachloride.

Each pyrazolone moiety in the title compound is nearly planar, but the C atoms of the phenyl groups are not coplanar with the pyrazolone rings (Table 1). The dihedral angle between the pyrazolone moieties is 110.9 (2)°. The crystal lattice is held together by hydrogen-bond interactions, forming dimeric units containing 16-membered rings (Fig. 2). The water molecule is linked to the carbonyl groups *via* hydrogen bonds (Table 2).

Experimental

4,4′-Methylenediantipyrine monohydrate was heated in acetone until most of the solid was dissolved. Crystals suitable for X-ray diffraction analysis were obtained by slow cooling of the solution containing a few drops of heptane.

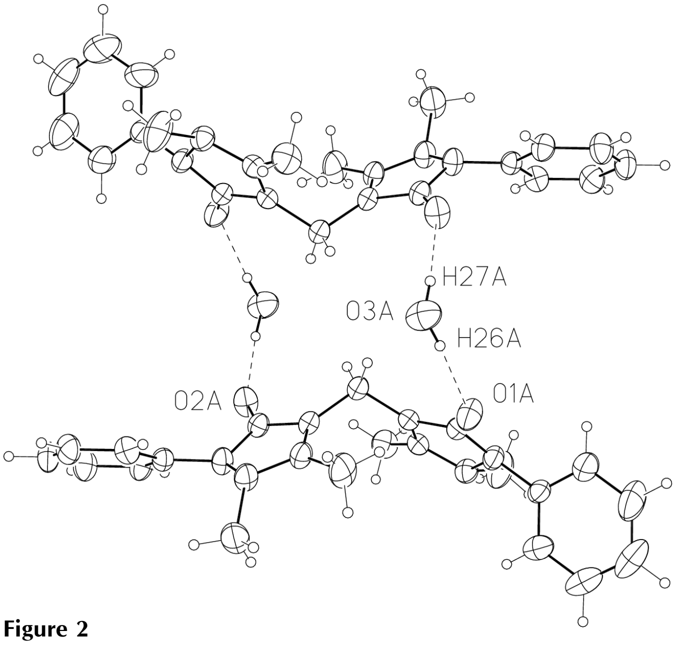


Figure 2
The dimeric units in the title compound, showing the hydrogen bonding between the water molecules and the carbonyl groups of the pyrazolone moieties.

Crystal data

$C_{23}H_{24}N_4O_2{\cdot}H_2O$
$M_r = 406.48$
Monoclinic, $P2_1/c$
$a = 11.937$ (3) Å
$b = 14.740$ (4) Å
$c = 12.085$ (3) Å
$\beta = 92.436$ (5)°
$V = 2124.4$ (10) Å^3
$Z = 4$

$D_x = 1.271$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 83 reflections
$\theta = 3.2$–19.7°
$\mu = 0.09$ mm^{-1}
$T = 203$ (2) K
Plate, colorless
0.4 × 0.3 × 0.1 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: empirical (Blessing, 1995)
$T_{\min} = 0.970$, $T_{\max} = 0.991$
12 780 measured reflections

3704 independent reflections
3017 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\max} = 25.0°$
$h = -12 \rightarrow 14$
$k = -17 \rightarrow 17$
$l = -14 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.130$
$S = 1.03$
3704 reflections
282 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0661P)^2 + 0.63P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C15	1.241 (2)	O3—H27	0.96 (3)
C1—N2	1.427 (2)	N4—C15	1.388 (2)
N1—C9	1.376 (2)	N4—C18	1.428 (2)
N1—N2	1.404 (2)	C7—C8	1.439 (2)
N1—C11	1.466 (3)	C8—C9	1.354 (2)
O2—C7	1.237 (2)	C8—C12	1.508 (2)
N2—C7	1.393 (2)	C9—C10	1.491 (3)
N3—C14	1.376 (2)	C12—C13	1.506 (2)
N3—N4	1.398 (2)	C13—C14	1.360 (2)
N3—C17	1.468 (2)	C13—C15	1.440 (2)
O3—H26	0.96 (3)	C14—C16	1.489 (3)
C9—N1—N2	106.05 (13)	C9—C8—C12	129.05 (16)
C7—N2—N1	109.09 (13)	C7—C8—C12	123.79 (15)
C7—N2—C1	124.86 (14)	C8—C9—N1	111.33 (15)
N1—N2—C1	118.49 (13)	C13—C12—C8	115.57 (14)
C14—N3—N4	106.09 (13)	C14—C13—C15	107.30 (15)
H26—O3—H27	109 (3)	C14—C13—C12	127.75 (16)
C15—N4—N3	109.70 (13)	C15—C13—C12	124.95 (15)
C15—N4—C18	124.83 (15)	C13—C14—N3	110.71 (16)
O2—C7—N2	122.85 (16)	O1—C15—N4	122.80 (16)
O2—C7—C8	131.11 (16)	O1—C15—C13	131.65 (16)
N2—C7—C8	106.01 (14)	N4—C15—C13	105.54 (15)
C9—C8—C7	107.03 (15)		
C9—N1—N2—C7	−7.34 (19)	C7—C8—C9—N1	−2.3 (2)
C9—N1—N2—C1	−158.51 (15)	N2—N1—C9—C8	5.9 (2)
C14—N3—N4—C15	8.37 (18)	C15—C13—C14—N3	3.87 (19)
C14—N3—N4—C18	162.43 (15)	N4—N3—C14—C13	−7.51 (19)
N1—N2—C7—O2	−171.97 (16)	N3—N4—C15—O1	173.24 (16)
C1—N2—C7—O2	−23.1 (3)	C18—N4—C15—O1	20.9 (3)
N1—N2—C7—C8	6.00 (18)	N3—N4—C15—C13	−6.04 (18)
C1—N2—C7—C8	154.90 (15)	C18—N4—C15—C13	−158.40 (16)
O2—C7—C8—C9	175.38 (18)	C14—C13—C15—O1	−177.80 (19)
N2—C7—C8—C9	−2.35 (18)	C14—C13—C15—N4	1.38 (18)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H26···O1	0.96 (3)	1.83 (3)	2.788 (2)	170 (3)
O3—H27···O2^{i}	0.96 (3)	1.84 (3)	2.789 (2)	175 (3)

Symmetry code: (i) $2 - x, 1 - y, 1 - z$.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Siemens, 1996); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans.* 2, pp. S1–19.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Minin, A. A. (1955). *Uch. Zap. Permsk. Gos. Univ.* **9**, 177–179.

Siemens (1996). *SHELXTL* (Version 5.10/DOS/WIN95/NT), *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc. Madison, Wisconsin, USA.

Singh, T. P. & Vijayan, M. (1973). *Acta Cryst.* B**29**, 714–720.

Vijayan, M. & Viswamitra, M. A. (1968). *Acta Cryst.* B**24**, 1067–1076.

Yuchi, A., Shiro, M., Wada, H. & Nakagawa, G. (1991). *Bull. Chem. Soc. Jpn*, **64**, 760–765.