Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,3-Dimethylquinoxaline–dimethylglyoxime (1/1)

Tuncer Hökelek,[a]* Hümeyra Batı,[b] Yunus Bekdemir[b] and Halil Kütük[b]

[a]Hacettepe University, Department of Physics, 06532 Beytepe, Ankara, Turkey, and [b]Ondokuz Mayıs University, Department of Chemistry, 55139 Kurupelit, Samsun, Turkey

Correspondence e-mail: merzifon@hacettepe.edu.tr

Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.002 Å
R factor = 0.046
wR factor = 0.133
Data-to-parameter ratio = 14.9

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

Received 22 June 2001
Accepted 27 June 2001
Online 6 July 2001

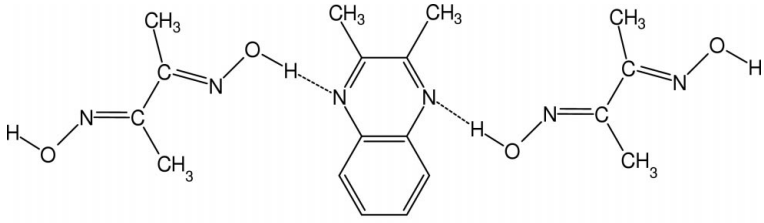
The title compound, $C_{10}H_{10}N_2{\cdot}C_4H_8N_2O_2$, consists of hydrogen-bonded 2,3-dimethylquinoxaline and dimethylglyoxime molecules. Both dimethylglyoximes are located on an inversion centre and there are two half-molecules in the asymmetric unit. The dimethylglyoxime molecules are linked about inversion centres to the 2,3-dimethylquinoxaline moiety by O—H···N hydrogen bonds (O···N 2.898 and 2.805 Å) to form polymeric chains.

Comment

Intermolecular hydrogen bonding has received considerable attention among the directional non-covalent intermolecular interactions (Etter *et al.*, 1990), which combines moderate strength and directionality (Karle *et al.*, 1996) in designing compounds to form supramolecular structures.

Oxime (–C═N-OH) groups possess stronger hydrogen-bonding capabilities than alcohols, phenols and carboxylic acids (Marsman *et al.*, 1999). The hydrogen-bond systems in the crystals of oximes have been analysed and a correlation between a pattern of hydrogen bonding and N—O bond lengths has been suggested (Bertolasi *et al.*, 1982). The configurational and/or conformational isomers of glyoxime derivatives (dioximes) have also been analysed (Chertanova *et al.*, 1994).

Oxime/oximato metal complexes have been investigated actively since the beginning of the last century of the millennium (Kukushkin & Pombeiro, 1999). In general, oxime and dioxime derivatives are very important compounds in the chemical industry and medicine. Dimethylglyoxime is actually the first selective organic reagent applied in the analysis of metals (Tshugaeff, 1905).



(I)

Crystals of dimethylglyoxime were reported by McCrone (1949) to be triclinic and its structure was undertaken by Merritt & Lanterman (1952). A neutron diffraction refinement of the crystal structure of dimethylglyoxime clarified the existence of the O—H (classical structure) bonding rather

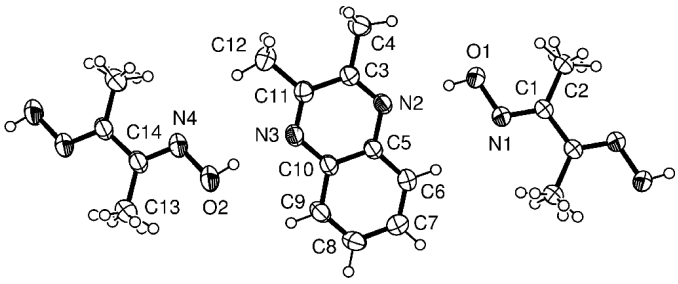


Figure 1
An *ORTEP*II (Johnson, 1976) drawing of the title molecule with the atom-numbering scheme. The displacement ellipsoids are drawn at the 50% probability level.

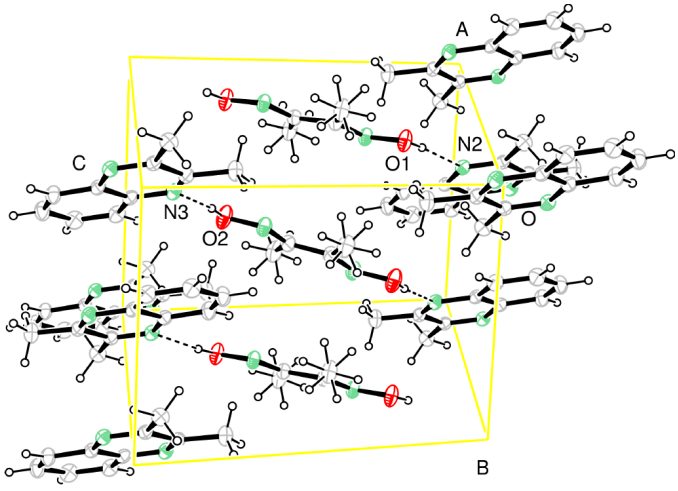


Figure 2
Packing diagram for (I). Hydrogen bonds are shown as dotted lines.

than N—H (zwitterion structure) (Hamilton, 1961).

Quinoxaline derivatives are very useful compounds with well known biological activities (Cheeseman & Werstiuk, 1978; Sato, 1996). Some of the quinoxaline derivatives act as *in vitro* anticancer compounds (Corona *et al.*, 1998). On the other hand, 2,3-dimethylquinoxaline is a polarographically active compound (Rodrigues *et al.*, 1997).

The structure of 2,3-dimethylquinoxaline was reported by Wozniak *et al.* (1990) to be monoclinic. The crystal structures containing 2,3-disubstituted derivatives of quinoxaline have aroused considerable interest because of the repulsions between the neighbouring substituents (Visser *et al.*, 1968; Visser & Vos, 1971; Lipkovski *et al.*, 1985; Krigier *et al.*, 1985).

The crystal structure determination of the title molecule, (I), was carried out in order to understand the strength of the hydrogen-bonding capabilities of the oxime groups having the classical (–C═N—O—H) structures. As shown in Fig. 1, the title compound, (I), consists of hydrogen-bonded 2,3-dimethylquinoxaline and dimethylglyoxime moieties. Both dimethylglyoximes are located on an inversion centre and there are two half-molecules in the asymmetric unit.

The bond lengths and angles of the 2,3-dimethylquinoxaline moiety are in accordance with the reported values (Woźniak *et al.*, 1990).

In the dimethylglyoxime moieties, the O—N, C═N, C—C bond lengths and C═N—O bond angles are larger, while the O—H, C—C′ bonds and N—O—H, C—C═N, C′–C═N angles are smaller than the corresponding ones reported in dimethylglyoxime (Hamilton, 1961) (Table 2). A comparison of the bond lengths and angles of the dimethylglyoxime moieties in the title compound, (I), with the corresponding ones in dimethylglyoxime, (II) (Hamilton, 1961), nickel dimethylglyoxime, (III) (Godycki & Rundle, 1953), copper dimethylglyoxime, (IV) (Frasson *et al.*, 1959) and acetoxime, (V) (Bierlein & Lingafelter, 1951), are given in Table 2.

As can be seen from the packing diagram (Fig. 2), there are intermolecular hydrogen bonds between the hydroxy H atoms of the dimethylglyoxime and N atoms of the 2,3-dimethylquinoxaline moieties (Table 3). The intermolecular hydrogen bonds are highly effective in forming the polymeric chains. Dipole-dipole and van der Waals interactions are also effective in the molecular packing.

An examination of the deviations from the least-squares planes through the individual rings shows that rings *A* (C5–C10) and *B* (C5/N2/C3/C11/N3/C10) are nearly planar with maximum deviations for the C5 [−0.007 (2) Å] and C5 [0.016 (2) Å] atoms, respectively.

Experimental

The title compound, (I), was prepared from a mixture of 2,3-butaneidone monoxime (2.02 g, 20.0 mmol), *o*-phenylenediamine (1.08 g, 10.0 mmol) and Na_2SO_4 (2.84 g, 20.0 mmol) in ethanol (30 ml). The mixture was heated at 343 K for 6 h. The solution was filtered and allowed to stand overnight in a refrigerator. The resulting precipitate was filtered and then recrystallized from 1,4-dioxane.

Crystal data

$C_{10}H_{10}N_2{\cdot}C_4H_8N_2O_2$
M_r = 274.32
Triclinic, $P\overline{1}$
a = 7.9814 (10) Å
b = 8.2719 (10) Å
c = 12.168 (3) Å
α = 91.779 (18)°
β = 106.668 (14)°
γ = 111.018 (10)°
V = 710.3 (2) Å^3
Z = 2
D_x = 1.283 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–11°
μ = 0.09 mm^{-1}
T = 294 (2) K
Rod, yellow
0.30 × 0.25 × 0.20 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Fair, 1990)
T_{min} = 0.974, T_{max} = 0.982
2884 measured reflections
2884 independent reflections
2244 reflections with $I > 2\sigma(I)$
θ_{max} = 26.3°
$h = 0 \rightarrow 9$
$k = -10 \rightarrow 9$
$l = -15 \rightarrow 14$
3 standard reflections
frequency: 120 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.133
S = 1.08
2884 reflections
193 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0745P)^2 + 0.0913P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C1—N1	1.2811 (18)	C14—N4	1.2813 (19)
C1—C1^{i}	1.477 (3)	C14—C14^{ii}	1.473 (3)
C1—C2	1.491 (2)	C14—C13	1.499 (2)
C3—N2	1.3119 (18)	N1—O1	1.4033 (16)
C5—N2	1.3723 (18)	N4—O2	1.3956 (18)
C10—N3	1.3676 (19)	O1—H1	0.85 (2)
C11—N3	1.3123 (19)	O2—H2	0.82 (2)
N1—C1—C1^{i}	115.18 (15)	C14^{ii}—C14—C13	120.72 (16)
N1—C1—C2	124.09 (13)	C1—N1—O1	112.39 (12)
C1^{i}—C1—C2	120.73 (15)	C3—N2—C5	118.23 (11)
N2—C3—C11	121.25 (12)	C11—N3—C10	118.35 (12)
N3—C11—C3	121.11 (13)	C14—N4—O2	112.15 (13)
N4—C14—C14^{ii}	115.03 (17)	N1—O1—H1	104.5 (14)
N4—C14—C13	124.25 (15)	N4—O2—H2	102.4 (16)
N2—C5—C10—N3	2.0 (2)	C2—C1—N1—O1	0.8 (2)
N2—C3—C11—N3	2.0 (2)	C13—C14—N4—O2	−0.8 (2)

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $1-x, 1-y, -1-z$.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N2^{i}	0.85	2.05	2.898	176
O2—H2···N3	0.82	1.99	2.805	173

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

Table 3
Comparison of the bond lengths (Å) and angles (°) in dimethylglyoxime moieties of (I) with the corresponding values in the related compounds (II), (III), (IV) and (V).

	(I)		(II)	(III)	(IV)	(V)
C1—C$_{trans}$	1.477 (3)	1.473 (3)	1.562 (18)	1.53	1.52	1.55
C1—C$_{cis}$	1.491 (2)	1.499 (2)	1.479 (15)	1.49	1.47	1.49
C1—N1	1.281 (2)	1.281 (2)	1.253 (11)	1.23	1.25	1.29
N1—O1	1.403 (2)	1.396 (2)	1.321 (21)	1.38	1.35	1.36
O1—H1	0.85 (2)	0.82 (2)	1.02 (4)	–	–	–
C$_{cis}$–C1—C$_{trans}$	120.7 (2)	120.7 (2)	120	123	122	117
N1—C1—C$_{trans}$	115.2 (2)	115.0 (2)	114	111	113	113
N1—C1—C$_{cis}$	124.1 (2)	124.3 (2)	126	127	125	131
C1—N1—O1	112.4 (2)	112.2 (2)	111	121	120	111
N1—O1—H1	104.5 (14)	102.4 (16)	110	102	–	–

The oxime H atoms were located from a difference map and refined isotropically; the positions of the remaining H atoms were calculated geometrically at distances of 0.93 (CH) and 0.96 Å (CH_3) from the corresponding C atoms, and a riding model was used during the refinement process. The H atoms of the C2 and C13 methyl groups are disordered.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *MolEN*.

The authors wish to acknowledge the purchase of a CAD-4 diffractometer under grant DPT/TBAG1 of the Scientific and Technical Research Council of Turkey.

References

Bertolasi, V., Gilli, G. & Veronese, A. C. (1982). *Acta Cryst.* B**38**, 502–511.
Bierlein, T. K. & Lingafelter, E. C. (1951). *Acta Cryst.* **4**, 450–453.
Cheeseman, G. W. H. & Werstiuk, E. S. G. (1978). *Adv. Heterocycl. Chem.* **22**, 367–431.
Chertanova, L., Pascard, C. & Sheremetev, A. (1994). *Acta Cryst.* B**50**, 708–716.
Corona, P., Vitale, G., Loriga, M., Paglietti, G. & Costi, M. P. (1998). *Il Farmaco*, **53**, 480–493.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Fair, C. K. (1990). *MolEN.* Enraf–Nonius, Delft, The Netherlands.
Frasson, E., Bardi, R. & Bezzi, S. (1959). *Acta Cryst.* **12**, 201–205.
Godycki, L. E. & Rundle, R. E. (1953). *Acta Cryst.* **6**, 487–495.
Hamilton, W. C. (1961). *Acta Cryst.* **14**, 95–100.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Karle, I. L., Ranganathan, D. & Haridas, V. (1996). *J. Am. Chem. Soc.* **118**, 7128–7133.
Kukushkin, V. Y. & Pombeiro, A. J. (1999). *Coord. Chem. Rev.* **181**, 147–175.
Krigier, C., Koçak, A. & Bekaroğlu, O. (1985). *Helv. Chim. Acta*, **68**, 581–582.
Lipkovski, J., Herbich, J. & Andreetti, G. D. (1985). 9th European Crystallography Meeting, Turin, Italy. Abstracts, pp.663–664.
Marsman, A. W., Leussing, E. D., Zwikker, J. W. & Jenneskens, L. W. (1999). *Chem. Mater.* **11**, 1484–1491.
McCrone, W. C. (1949). *Anal. Chem.* **21**, 1428–1429.
Merritt, L. L. Jr & Lanterman, E. (1952). *Acta Cryst.* **5**, 811–817.
Rodrigues, J. A., Barros, A. A., Cruz, J. M. M. & Ferreira, A. A. (1997). *J. Inst.* Brewing, **103**, 311–314.
Sato, N. (1996). In *Comprehensive Heterocyclic Chemistry* II, Vol. 6, edited by A. R. Katritzky, C. W. Rees & E. F. V. Scriven, pp. 233–278. Oxford: Pergamon.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.
Tshugaeff, L. (1905). *Z. Anorg. Chem.* **46**, 144.
Visser, G. J. & Vos, A. (1971). *Acta Cryst.* B**27**, 1793–1801.
Visser, G. J., Vos, A., De Grooth, A. & Wynberg, H. (1968). *J. Am. Chem. Soc.* **90**, 3253–3254.
Woźniak, K., Krygowski, T. M., Kariuki, B. & Jones, W. (1990). *Acta Cryst.* C**46**, 1946–1947.