Fig. 1, generated with *STRUPLO84* (Fischer, 1985), shows a projection along the $b$ axis of the atomic arrangement of this salt.

### References


ADAMS, J. M. & RAMDAS, V. (1977). *Acta Cryst.* **B33**, 3654–3657.
ADAMS, J. M. & SMALL, R. W. H. (1974). *Acta Cryst.* **B30**, 2191–2193.
CORBRIDGE, D. E. C. (1974). *The Structural Chemistry of Phosphorus*, pp. 227–234. Amsterdam: Elsevier.
Enraf–Nonius (1977). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.
FISCHER, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
ILYUKHIN, V. V., KALININ, V. R., KUVSHINOVA, T. B. & TANANAEV, I. V. (1981). *Dokl. Akad. Nauk SSSR*, **266**, 1387–1391.
ILYUKHIN, V. V., KALININ, V. R., KUVSHINOVA, T. B. & TANANAEV, I. V. (1982). *Dokl. Akad. Nauk SSSR*, **267**, 85–88.
KUVSHINOVA, T. B., WOLF, G. U. & MEISEL, M. (1984). *Izv. Akad. Nauk SSSR Neorg. Mater.* **20**, 1056–1062.
MAIN, P., LESSINGER, L., WOOLFSON, M. M., GERMAIN, G. & DECLERCQ, J.-P. (1977). *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
NIKOLAEV, V. P. & KUVSHINOVA, T. B. (1987). *Izv. Akad. Nauk SSSR Neorg. Mater.* **23**, 622–625.
WOLF, G. U. & MEISEL, M. (1978). *Z. Chem.* **18**, 377.


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# Structure of (*E*)-Phenyl 2-Pyridyl Ketone Oxime

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**Abstract.** $C_{12}H_{10}N_2O$, $M_r = 198{\cdot}2$, monoclinic, $C2/c$, $a = 16{\cdot}246$ (3), $b = 8{\cdot}423$ (1), $c = 17{\cdot}383$ (3) Å, $\beta = 122{\cdot}34$ (1)°, $V = 2009{\cdot}7$ (1) Å$^3$, $Z = 8$, $D_x = 1{\cdot}31$, $D_m = 1{\cdot}30$ g cm$^{-3}$, $\lambda$(Cu $K\alpha$) = 1·54178 Å, $\mu = 6{\cdot}53$ cm$^{-1}$, $F(000) = 832$, $T = 295$ K, $R(F) = 0{\cdot}045$ for 1357 independent reflections. The molecules form a unique centrosymmetric dimer, in which the OH group forms a bifurcated hydrogen bond with the pyridine N atom and the oxime N atom. The two oxime N atoms in the dimer have a short nonbonding contact 2·837 (4) Å.

**Introduction.** The crystal structure of the title compound was determined as part of our studies of ketone oxime derivatives (Taga & Miyasaka, 1987; Taga, Uchiyama, Machida & Miyasaka, 1988). One of the characteristics of an oxime compound is dimer formation through OH···N hydrogen bonds as observed in several oxime derivatives, *e.g.* *p*-nitrobenzaldehyde oxime (Brehm & Watson, 1972; Bachechi & Zambonelli, 1973), *p*-dimethylaminobenzaldehyde oxime (Bachechi & Zambonelli, 1972), 1-phenyl-1,2-propanedione 2-oxime (Saarinen, Korvenranta & Nasakkala, 1977) and carvoxime (Oonk & Kroon, 1976; Kroon, van Gurp, Oonk, Baert & Fouret, 1976). The hydrogen bonds are usually formed between the N—OH groups related by a center of symmetry. Stability of such a hydrogen-bonding system was theoretically studied by Jeffrey, Ruble, McMullan, DeFrees & Pople (1981) and Jeffrey, Ruble & Pople (1982). The title ketone oxime forms a similar centrosymmetric dimer, but the hydrogen bonds are of a bifurcated type. This paper describes the details of the structure of the unique hydrogen-bonded dimer.

**Experimental.** Crystals from ethanol–water as colorless prisms; crystal dimensions 0·2 × 0·2 × 0·3 mm; density by flotation; Rigaku AFC-5RU diffractometer with graphite monochromator; cell dimensions by least-squares to fit 20 $\theta$ angles (16·2–28·3°); 1442 reflections ($0 \le h \le 18$, $0 \le k \le 9$, $-19 \le l \le 19$) collected within $2\theta < 120°$; $2\theta$–$\omega$ scan mode; intensity fluctuation less than 2% for three standard reflections measured every 56 reflections; intensities corrected for Lorentz and polarization factors, but not for absorption; 1357 unique reflections with $F_o > 3\sigma(F_o)$ used for structure determination. Structure solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refined by full-matrix least squares based on $F$; $w = [\sigma^2(F) + (0{\cdot}023F)^2]^{-1}$; non-H atoms anisotropic, H atoms found in difference maps were isotropic; $R = 0{\cdot}045$, $wR = 0{\cdot}071$; $S = 1{\cdot}4$; maximum parameter shift less than $0{\cdot}05\sigma$; maximum residual density 0·25 e Å$^{-3}$; atomic scattering factors from *International Tables*

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Table 1. *Atomic coordinates and equivalent isotropic temperature factors*

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$)* |
|---|---|---|---|---|
| N(1) | 0·5523 (1) | 0·3553 (2) | 0·5196 (1) | 3·96 (5) |
| C(2) | 0·5867 (1) | 0·2547 (2) | 0·5844 (1) | 3·57 (6) |
| C(3) | 0·5117 (1) | 0·1808 (2) | 0·5970 (1) | 3·70 (6) |
| C(4) | 0·5179 (1) | 0·0212 (2) | 0·6209 (1) | 4·62 (8) |
| C(5) | 0·4465 (2) | −0·0439 (2) | 0·6303 (2) | 5·24 (9) |
| C(6) | 0·3702 (1) | 0·0508 (3) | 0·6173 (2) | 5·06 (8) |
| C(7) | 0·3701 (1) | 0·2067 (3) | 0·5953 (1) | 4·69 (7) |
| N(8) | 0·4379 (1) | 0·2736 (2) | 0·5846 (1) | 4·11 (5) |
| C(9) | 0·6904 (1) | 0·2067 (2) | 0·6471 (1) | 3·51 (6) |
| C(10) | 0·7292 (1) | 0·2077 (2) | 0·7404 (1) | 4·53 (8) |
| C(11) | 0·8241 (2) | 0·1579 (3) | 0·8006 (1) | 5·34 (8) |
| C(12) | 0·8799 (1) | 0·1062 (3) | 0·7688 (2) | 5·42 (8) |
| C(13) | 0·8430 (1) | 0·1053 (2) | 0·6768 (2) | 5·18 (9) |
| C(14) | 0·7481 (1) | 0·1573 (2) | 0·6156 (1) | 4·27 (7) |
| O(15) | 0·6235 (1) | 0·4296 (2) | 0·5101 (1) | 4·40 (5) |

* $B_{eq} = \frac{4}{3}\sum_i\sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j$.

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

| | | | |
|---|---|---|---|
| N(1)—C(2) | 1·276 (2) | N(1)—O(15) | 1·400 (3) |
| C(2)—C(3) | 1·485 (3) | C(2)—C(9) | 1·492 (2) |
| C(3)—C(4) | 1·395 (3) | C(3)—N(8) | 1·349 (3) |
| C(4)—C(5) | 1·369 (4) | C(5)—C(6) | 1·388 (3) |
| C(6)—C(7) | 1·368 (3) | C(7)—N(8) | 1·335 (3) |
| C(9)—C(10) | 1·391 (3) | C(9)—C(14) | 1·378 (4) |
| C(10)—C(11) | 1·387 (3) | C(11)—C(12) | 1·362 (4) |
| C(12)—C(13) | 1·375 (4) | C(13)—C(14) | 1·395 (3) |
| C(2)—N(1)—O(15) | 113·7 (1) | N(1)—C(2)—C(3) | 113·8 (1) |
| N(1)—C(2)—C(9) | 127·9 (2) | C(3)—C(2)—C(9) | 118·3 (2) |
| C(2)—C(3)—C(4) | 120·9 (2) | C(2)—C(3)—N(8) | 117·6 (2) |
| C(4)—C(3)—N(8) | 121·5 (2) | C(3)—C(4)—C(5) | 119·4 (2) |
| C(4)—C(5)—C(6) | 119·4 (2) | C(5)—C(6)—C(7) | 117·6 (2) |
| C(6)—C(7)—N(8) | 124·6 (2) | C(3)—N(8)—C(7) | 117·5 (2) |
| C(2)—C(9)—C(10) | 118·6 (2) | C(2)—C(9)—C(14) | 122·3 (2) |
| C(10)—C(9)—C(14) | 119·0 (2) | C(9)—C(10)—C(11) | 120·3 (2) |
| C(10)—C(11)—C(12) | 120·3 (2) | C(11)—C(12)—C(13) | 120·2 (2) |
| C(12)—C(13)—C(14) | 120·1 (3) | C(9)—C(14)—C(13) | 120·1 (2) |

*for X-ray Crystallography* (1974, Vol. IV); computations performed on a FACOM M780 in the Data Processing Center of Kyoto University, using the program *KPPXRAY* (Taga, Higashi & Iizuka, 1985).

**Discussion.** Atomic coordinates are given in Table 1.* Bond distances and bond angles are given in Table 2. A perspective view of the centrosymmetric dimer is shown in Fig. 1. The C—C bond distances and angles show no large deviations from the usual values. The C(2)═N(1) bond distance is close to that of other ketone oximes, and the N(1)—O(15) distance is also normal in comparison with those of the N—OH oximes, for which a possible relation to hydrogen bonding has been suggested (Bertolasi, Gilli & Veronese, 1982; Jerslev, 1983). The OH group forms a bifurcated hydrogen bond with the pyridine N atom and the oxime N atom. The OH···N(oxime) hydrogen bond corresponds to that observed in other oxime dimers. The O···N(oxime) distance 3·183 (2) Å [H···N = 2·57 (1) Å and O—H···N = 118 (2)°] is, however, quite long, while the OH···N(pyridine) distance 2·863 (2) Å [H···N = 1·86 (1) Å, O—H···N = 164 (2)°, and O—H = 1·03 (2) Å] is shorter than the former; it is slightly longer than the 2·708–2·751 Å of similar hydrogen bonds observed in non-dimer oximes, 4-pyridinecarboxaldehyde oxime (Martinez-Ripoll & Lorenz, 1976*a*,*b*), 4-pyrimidinecarboxyaldehyde oxime (Martinez-Ripoll & Lorenz, 1973, 1974) and 3-fluoro-4-pyridinecarboxaldehyde oxime (Sorof, Carrell, Glusker, McLick & Kun, 1985). The two oxime N atoms in the dimer have a very short intermolecular contact 2·863 (2) Å. This contact lengthens the OH···N(oxime) hydrogen bonds. The >C═N—O group [O(15), N(1), C(2), C(3) and C(9)] is planar within 0·02 Å, and the two >C═N—O planes in the dimer are not coplanar; the oxime N atom and the pyridine N atom of another molecule deviate from the >C═N—O plane by 1·73 (4) and 0·96 (4) Å, respectively. Such a displacement between the two >C═N—O planes decreases the N(oxime)···N(oxime) repulsive forces between their lone-pair electrons stretching approximately on the plane.

Usually aldoximes having one aromatic ring take a planar conformation owing to the resonance effect between the oxime double bond and the aromatic ring conjugation. However, the pyridine and phenyl rings of the present ketone oxime tilt from the oxime plane by 37·4 (1) and 51·7 (1)°, respectively, and both rings have a large dihedral angle 73·3 (1)°. The orientation of the pyridine ring with an

* Lists of atomic parameters for H atoms, anisotropic thermal parameters for non-H atoms and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53111 (6 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

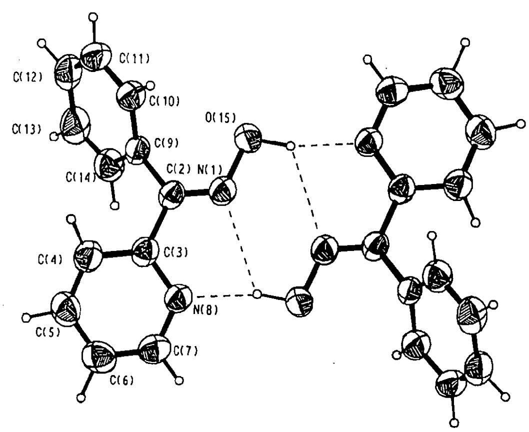


Fig. 1. Drawing of the centrosymmetric dimer with the atom-numbering scheme and thermal ellipsoids depicted at the 50% probability level.

N(8)—C(3)—C(2)—N(1) angle −37·5 (2)° differs from that observed in other phenyl 2-pyridyl ketone oximes (Taga & Miyasaka, 1987; Taga, Uchiyama, Machida & Miyasaka, 1988), in which the pyridine N atom locates near the phenyl ring. From the viewpoint of non-bonding interactions between the aromatic rings, the orientation of the present pyridine ring is unfavorable, because the C(14)H···HC(4) repulsions between the rings may be larger than C(14)H···N repulsions. However, this orientation brings the pyridine N atom to a favorable position for the formation of the OH···N(pyridine) hydrogen bond.

### References


BACHECHI, F. & ZAMBONELLI, L. (1972). *Acta Cryst.* **B28**, 2489–2494.

BACHECHI, F. & ZAMBONELLI, L. (1973). *Acta Cryst.* **B29**, 2598–2600.

BERTOLASI, V., GILLI, G. & VERONESE, A. C. (1982). *Acta Cryst.* **B38**, 502–511.

BREHM, L. & WATSON, K. J. (1972). *Acta Cryst.* **B28**, 3646–3652.

JEFFREY, G. A., RUBLE, J. R., MCMULLAN, R. K., DEFREES, D. J. & POPLE, J. A. (1981). *Acta Cryst.* **B37**, 1381–1387.

JEFFREY, G. A., RUBLE, J. R. & POPLE, J. A. (1982). *Acta Cryst.* **B38**, 1975–1980.

JERSLEV, B. (1983). *Acta Cryst.* **C39**, 1447–1454.

KROON, J., VAN GURP, P. R. E., OONK, H. A. J., BAERT, F. & FOURET, R. (1976). *Acta Cryst.* **B32**, 2561–2564.

MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

MARTINEZ-RIPOLL, M. & LORENZ, H. P. (1973). *Acta Cryst.* **B29**, 2260–2263.

MARTINEZ-RIPOLL, M. & LORENZ, H. P. (1974). *Acta Cryst.* **B30**, 793–796.

MARTINEZ-RIPOLL, M. & LORENZ, H. P. (1976*a*). *Acta Cryst.* **B32**, 2322–2325.

MARTINEZ-RIPOLL, M. & LORENZ, H. P. (1976*b*). *Acta Cryst.* **B32**, 2325–2328.

OONK, H. A. J. & KROON, J. (1976). *Acta Cryst.* **B32**, 500–504.

SAARINEN, H., KORVENRANTA, J. & NASAKKALA, E. (1977). *Cryst. Struct. Commun.* **6**, 557–559.

SOROF, J. M., CARRELL, H. L., GLUSKER, J. P., MCLICK, J. & KUN, E. (1985). *Acta Cryst.* **C41**, 785–788.

TAGA, T., HIGASHI, T. & IIZUKA, H. (1985). *KPPXRAY. Kyoto Program Package for X-ray Crystal Structure Analysis.* Kyoto Univ., Japan.

TAGA, T. & MIYASAKA, T. (1987). *Acta Cryst.* **C43**, 748–751.

TAGA, T., UCHIYAMA, A., MACHIDA, K. & MIYASAKA, T. (1988). *Acta Cryst.* **C44**, 2185–2186.


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# Structure of *o*-Toluenesulfonic Acid Dihydrate

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**Abstract.** $C_7H_7SO_3^-.H_5O_2^+$, $M_r = 208·2$, orthorhombic, $Pca2_1$ (No. 29), $a = 9·565$ (1), $b = 8·694$ (1), $c = 11·866$ (2) Å, $V = 986·8$ (1) Å$^3$, $Z = 4$, $D_x = 1·401$ g cm$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71069 Å, $\mu = 3·03$ cm$^{-1}$, $F(000) = 440$, $T = 296$ K, $R = 0·037$ for 1436 reflections. The benzene ring is distorted by the *ortho* substituent, and the sulfonate group has a usual orientation to the ring. Two water molecules form an $H_5O_2^+$ cation with a short hydrogen bond [2·425 (3) Å], and the cation looks like an aquaoxonium ion with the pyramidal $H_3O^+$ ion bonded to the normal $H_2O$ molecule.

**Introduction.** Several types of hydrogen bonding around a hydronium ion have been reported so far (Lundgren & Olovsson, 1976). The $H_5O_2^+$ cation in picrylsulfonic acid tetrahydrate has a *gauche* type (Lundgren & Tellgren, 1974), while that in *o*-sulfobenzoic acid trihydrate has a *cis* type (Attig & Mootz, 1976). In the present work, the hydrogen bonding in the title crystal as a hydrated proton complex of the strong sulfonic acid has been determined.

**Experimental.** A prismatic translucent crystal obtained from aqueous solution was mounted on a Rigaku AFC-5RU diffractometer; dimensions were 0·4 × 0·4 × 0·5 mm. Cell dimensions were determined by a least-squares method from the setting angles of 20 reflections having $16 < \theta < 20°$. Intensity data of 1470 reflections ($0 \leq h \leq 12$, $0 \leq k \leq 12$, $0 \leq l \leq 16$) were collected within $2\theta < 60°$, using graphite-monochromated Mo $K\alpha$ radiation; $2\theta$–$\omega$ scans at speeds of 4° min$^{-1}$ were made over a range of $(0·7 + 0·45\tan\theta)°$. Three check reflections showed no significant fluctuation during data collection. Data were corrected for Lorentz and polarization factors, but not for absorption. Structure solved with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), and refined by full-

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