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## Resonance-Assisted Hydrogen Bonds Between Oxime and Carboxyl Groups. II. The Tetrameric Structure of Pyruvic Acid Oxime

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### Abstract

Pyruvic acid oxime (2-hydroxyiminopropanoic acid),  $C_3H_5NO_3$ , is a molecule in which  $\pi$  resonance between the carboxyl and oxime groups might occur. The  $\pi$ -electron interaction affects the hydrogen-bond dimensions. Hydrogen-bonded cyclic tetramers of molecules are observed. Only  $OH \cdots N$  and  $OH \cdots O$  hydrogen bonds between the oxime and carboxyl groups are observed.

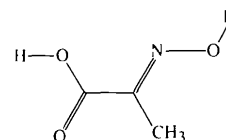
### Comment

Oximes of oxocarboxylic acids (molecules which contain both the carboxyl and oxime group) are examples of compounds that form very stable hydrogen bonds (Maurin, Paul & Curtin, 1992*a,b*, 1994). In the simple reaction of aldehydes and ketones with hydroxylamine hydrochloride in alkaline solution (Fuson, 1962), the *E* isomers of oximes are obtained in prevalence over the *Z* isomers. As was shown by Gieren, Hübner & Ruiz-Perez (1986*a,b*) for acetophenone oxime, the *E* form exists in a crystalline state in centrosymmetric dimeric arrangements, unlike the *Z* isomer which forms chain structures. The stability of such dimers, which can also be observed in solutions, is explained as a result of engagement of pairs of hydrogen bonds in dimer formation. The same is true for carboxylic acid dimers.

In the *E* isomers of the oximes with a carboxyl group as the second functionality, pairs of hydrogen bonds linking the molecules have also been observed (Maurin *et al.*, 1992*a,b*, 1994; Padmanabhan, Paul & Curtin, 1989). Unlike carboxylic acid or oxime dimers, the molecules of this type are linked *via* oxime–carboxyl hydrogen bonds, generating chain structures. Another structure type has been observed for 4-methyl-2-oxopentanoic acid oxime and levulinic acid oxime (Maurin, Leś & Winnicka-Maurin, 1995), the molecules of which form cyclic tetramers. For these compounds also, the same  $OH \cdots N$  and  $OH \cdots O$  hydrogen bonds between oxime and carboxyl groups were observed. Apart from a seemingly alike packing scheme for both

structures, they showed differences in hydrogen-bond dimensions, which were explained as due to  $\pi$  resonance for 4-methyl-2-oxopentanoic acid oxime and the lack of this effect for levulinic acid oxime. The discussion was based on the comparison of structural data and results of *ab initio* quantum-mechanical calculations both for isolated molecules of model compounds and for model structures of hydrogen-bonded dimers. The pyruvic acid oxime was employed in both cases as a model compound for 4-methyl-2-oxopentanoic acid oxime.

The present study was performed mainly for two reasons: (i) to check if the model compound really forms a tetrameric structure like 4-methyl-2-oxopentanoic acid oxime, and (ii) to determine the crystal data for the model structure in order to clarify some uncertainties concerning the previously observed structure with partial disorder (Maurin *et al.*, 1995).



The title compound formed the expected tetramer (Fig. 1). There are, however, some differences between this structure and those studied previously (Maurin *et al.*, 1995). While all three structures are centrosymmetric (levulinic acid oxime, space group  $P2_1/c$ ; 4-methyl-2-oxopentanoic acid oxime,  $P1$ ; pyruvic acid oxime,  $P1$ ), the tetramers themselves are non-centrosymmetric in the present structure. This means that unlike in the two previous structures, we now observe four molecules of different geometry instead of the previous two. Molecule (I) is not planar, the oxime and carboxyl groups being rotated by *ca*  $9^\circ$  around the C11—C12 bond (Table 3), whereas the other three molecules are almost planar. It is worth noting that the functional groups of the adjacent hydrogen-bonded molecules (II), (III) and (IV) are also almost coplanar. The distortions of the conjugated  $\pi$ -electron system in (I) are negligible, resulting in small discrepancies between the bond lengths of (I) and the other three molecules.

The tetramers form almost planar sheets parallel to (110) with an interplanar distance of 3.283 (5) Å. The crystal packing is shown in Fig. 2. The hydrogen-bond dimensions are in good agreement with the values observed for 4-methyl-2-oxopentanoic acid oxime (Maurin *et al.*, 1995). The mean value of the  $OH \cdots N$  bond length is 2.755 (3) Å, and that of  $OH \cdots O$  is 2.686 (2) Å [2.773 (3) and 2.670 (3) Å, respectively, for 4-methyl-2-oxopentanoic acid oxime]. The shortening of the  $OH \cdots O$  and the lengthening of the  $OH \cdots N$  hydrogen bonds compared with the values observed for the levulinic acid oxime may be caused by the  $\pi$  resonance between the two functional groups (Maurin *et al.*, 1995, and references therein).

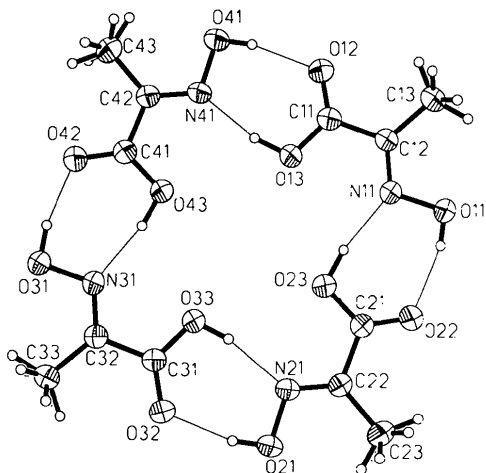


Fig. 1. Hydrogen-bonded cyclic tetramer and the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

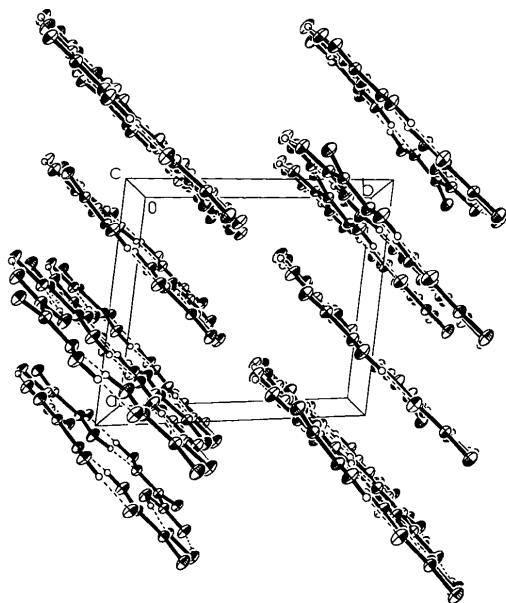


Fig. 2. View of the crystal packing along the *c* axis.

## Experimental

Pyruvic acid oxime was obtained by the standard reaction of pyruvic acid and hydroxylamine hydrochloride in alkaline solution (Fuson, 1962). The compound was purified by recrystallization from water/ethanol solution. The colourless columnar crystals suitable for data collection were obtained from methyl ether solution by slow evaporation.

### Crystal data

C<sub>3</sub>H<sub>5</sub>NO<sub>3</sub>  
*M<sub>r</sub>* = 103.08

Cu K $\alpha$  radiation  
 $\lambda$  = 1.54178 Å

### Triclinic

*P* $\bar{1}$   
*a* = 8.313 (5) Å  
*b* = 9.717 (5) Å  
*c* = 12.151 (4) Å  
 $\alpha$  = 70.86 (4)°  
 $\beta$  = 88.56 (4)°  
 $\gamma$  = 82.11 (5)°  
*V* = 918.3 (8) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.491 Mg m<sup>-3</sup>

### Data collection

Kuma KM-4  $\kappa$ -axis four-circle diffractometer  
 Profile data from  $\omega/\theta$  scans  
 Absorption correction: none  
 2863 measured reflections  
 2654 independent reflections  
 1875 observed reflections  
 [*I* > 2 $\sigma$ (*I*)]

### Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2 $\sigma$ (*F*<sup>2</sup>)] = 0.0393  
*wR*(*F*<sup>2</sup>) = 0.1038  
*S* = 1.130  
 2654 reflections  
 294 parameters  
 $w = 1/[\sigma^2(F_o^2) + (0.0741P)^2 + 0.1438P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.318 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.231 \text{ e \AA}^{-3}$

### Cell parameters from 25 reflections

$\theta$  = 16–18°  
 $\mu$  = 1.183 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Columnar  
 0.5 × 0.25 × 0.2 mm  
 Colourless

*R*<sub>int</sub> = 0.0174

$\theta_{\max}$  = 60.05°

*h* = -9 → 0

*k* = -10 → 10

*l* = -13 → 13

3 standard reflections

monitored every 200

reflections

intensity decay: none

### Extinction correction:

*SHELXL93* (Sheldrick, 1993)

### Extinction coefficient:

0.0056 (8)

### Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
N11	0.1484 (2)	0.1133 (2)	0.37383 (13)	0.0412 (4)
O11	0.1831 (2)	0.0731 (2)	0.49130 (11)	0.0527 (4)
O12	-0.1154 (2)	0.36990 (15)	0.17116 (12)	0.0503 (4)
O13	0.0693 (2)	0.1866 (2)	0.15574 (12)	0.0529 (4)
C11	-0.0137 (2)	0.2643 (2)	0.2137 (2)	0.0405 (5)
C12	0.0256 (2)	0.2128 (2)	0.3408 (2)	0.0377 (5)
C13	-0.0763 (3)	0.2809 (2)	0.4163 (2)	0.0499 (6)
N21	0.5726 (2)	-0.2840 (2)	0.26620 (14)	0.0419 (4)
O21	0.6884 (2)	-0.3971 (2)	0.25968 (13)	0.0554 (4)
O22	0.4282 (2)	-0.1314 (2)	0.47422 (12)	0.0561 (4)
O23	0.3526 (2)	-0.0765 (2)	0.28761 (12)	0.0508 (4)
C21	0.4419 (2)	-0.1518 (2)	0.3812 (2)	0.0393 (5)
C22	0.5652 (2)	-0.2718 (2)	0.3675 (2)	0.0396 (5)
C23	0.6665 (3)	-0.3655 (3)	0.4703 (2)	0.0573 (6)
N31	0.3297 (2)	-0.0971 (2)	-0.16378 (13)	0.0398 (4)
O31	0.2825 (2)	-0.0651 (2)	-0.27864 (11)	0.0498 (4)
O32	0.6054 (2)	-0.3442 (2)	0.03534 (12)	0.0557 (4)
O33	0.4225 (2)	-0.1590 (2)	0.04902 (12)	0.0513 (4)
C31	0.4983 (2)	-0.2436 (2)	-0.0067 (2)	0.0398 (5)
C32	0.4419 (2)	-0.2062 (2)	-0.1295 (2)	0.0386 (5)
C33	0.5183 (3)	-0.2939 (2)	-0.2014 (2)	0.0506 (6)
N41	-0.0682 (2)	0.3177 (2)	-0.06230 (14)	0.0434 (4)
O41	-0.1823 (2)	0.4333 (2)	-0.05748 (14)	0.0556 (4)
O42	0.0624 (2)	0.1553 (2)	-0.26732 (12)	0.0538 (4)

O43	0.1423 (2)	0.1025 (2)	-0.08178 (12)	0.0516 (4)
C41	0.0532 (2)	0.1785 (2)	-0.1751 (2)	0.0403 (5)
C42	-0.0647 (2)	0.3016 (2)	-0.1618 (2)	0.0396 (5)
C43	-0.1683 (3)	0.3938 (2)	-0.2643 (2)	0.0533 (6)

Table 2. Selected bond lengths (Å) and angles (°)

N11—C12	1.278 (3)	N31—C32	1.275 (2)
N11—O11	1.378 (2)	N31—O31	1.381 (2)
O12—C11	1.212 (2)	O32—C31	1.211 (2)
O13—C11	1.313 (2)	O33—C31	1.316 (2)
C11—C12	1.489 (3)	C31—C32	1.487 (3)
C12—C13	1.484 (3)	C32—C33	1.485 (3)
N21—C22	1.273 (2)	N41—C42	1.269 (2)
N21—O21	1.380 (2)	N41—O41	1.383 (2)
O22—C21	1.210 (2)	O42—C41	1.212 (2)
O23—C21	1.314 (2)	O43—C41	1.313 (2)
C21—C22	1.493 (3)	C41—C42	1.488 (3)
C22—C23	1.482 (3)	C42—C43	1.485 (3)
C12—N11—O11	113.0 (2)	C32—N31—O31	113.0 (2)
O12—C11—O13	125.0 (2)	O32—C31—O33	124.7 (2)
O12—C11—C12	120.5 (2)	O32—C31—C32	121.0 (2)
O13—C11—C12	114.5 (2)	O33—C31—C32	114.3 (2)
N11—C12—C13	126.2 (2)	N31—C32—C33	125.7 (2)
N11—C12—C11	115.2 (2)	N31—C32—C31	115.0 (2)
C13—C12—C11	118.6 (2)	C33—C32—C31	119.4 (2)
C22—N21—O21	112.7 (2)	C42—N41—O41	112.4 (2)
O22—C21—O23	124.8 (2)	O42—C41—O43	124.8 (2)
O22—C21—C22	120.0 (2)	O42—C41—C42	120.2 (2)
O23—C21—C22	115.2 (2)	O43—C41—C42	115.0 (2)
N21—C22—C23	125.8 (2)	N41—C42—C43	125.6 (2)
N21—C22—C21	115.7 (2)	N41—C42—C41	116.3 (2)
C23—C22—C21	118.5 (2)	C43—C42—C41	118.1 (2)

Table 3. Selected dihedral angles (°)

Plane *A* is defined by atoms O<sub>x</sub>2, O<sub>x</sub>3, C<sub>x</sub>1 and C<sub>x</sub>2, and plane *B* is defined by atoms C<sub>x</sub>1, C<sub>x</sub>2, N<sub>x</sub>1 and O<sub>x</sub>1, where *x* is 1, 2, 3 and 4 for molecules (I), (II), (III) and (IV), respectively.

A(I) ^ B(I)	8.4 (3)	A(III) ^ B(III)	0.6 (3)
B(I) ^ A(II)	9.4 (3)	B(III) ^ A(IV)	0.1 (3)
A(II) ^ B(II)	1.6 (2)	A(IV) ^ B(IV)	0.8 (2)
B(II) ^ A(III)	3.2 (2)	B(IV) ^ A(I)	6.9 (2)

All non-H atoms were found from an *E* map. Most of the H atoms were localized from the  $\Delta\rho$  map including those of the disordered methyl groups. All non-H atoms were refined with anisotropic displacement parameters. The oxime and carboxyl H atoms were refined with isotropic displacement parameters, whereas the disordered methyl H atoms were placed in calculated positions and their site occupation and isotropic displacement parameters refined.

Data collection: Kuma KM-4 system (Kuma, 1991). Cell refinement: Kuma KM-4 system. Data reduction: Kuma KM-4 system. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1262). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## Five-, Six- and Seven-Membered-Ring Substituted Thiazolidine-2-thione

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## Abstract

The X-ray structures of 3,3a,4,5,6,6a-hexahydro-2H-cyclopenta[d]thiazole-2-thione, (1), 3-methyl-2,3,3a,4,5,6,7,7a-octahydrobenzo[d]thiazole-2-thione, (2), and 3,3a,4,5,6,7,8,8a-octahydro-2H-cyclohepta[d]thiazole-2-thione, (3), are presented. The condensation of a five-, six- or seven-membered ring onto the C4—C5 bond of a thiazolidine-2-thione ring does not affect the flexibility of the heteroatomic ring, which adopts different