

Resonance-Assisted Hydrogen Bonds Between Oxime and Carboxyl Group. Comparison of Tetrameric Structures of 4-Methyl-2-oxopentanoic Acid Oxime and Levulinic Acid Oxime

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Abstract

Crystal structures of oximes of two aliphatic keto-carboxylic acids, 4-methyl-2-oxopentanoic acid oxime [(PEN) 4-methyl-2-(hydroxylimino)pentanoic acid] and levulinic acid oxime [(LEV) 4-(hydroxylimino)pentanoic acid], were determined by X-ray structural methods. The molecular structures of monomers interacting *via* hydrogen-bond networks were analysed with the use of theoretical *ab initio* self-consistent field (SCF) calculations on model systems. The results of present crystallographic and theoretical studies show that a different structure of PEN and LEV crystals originates mostly from electron charge distribution, depending on the relative position of the oxime and carboxyl moieties. The observed N—O and N=C bond lengths and O—H...N and O—H...O hydrogen-bond contacts in PEN crystals are affected by the π -electron resonance of the oxime and carboxyl moieties in a way similar to that found in β -diketones.

Introduction

Simple organic molecules possessing two functional groups of both donor and acceptor capabilities in hydrogen-bond formation exhibit several interesting physical and chemical properties. The molecular crystals of these molecules usually consist of infinite polar chains (Maurin, Paul & Curtin, 1992*a,b,c,d*, 1994). If the crystallization occurs in polar space groups, it is accompanied by several interesting physical phenomena such as pyroelectricity or triboluminescence, pyroelectric luminescence and piezoelectricity under hydrostatic pressure (Padmanabhan, Paul & Curtin, 1989; Hahn & Klapper, 1983; Lang, 1974; Hardy, Kaska, Chandra &

Zink, 1981; Chandra & Zink, 1980). Other features, such as second-harmonic generation and piezoelectricity, occur for almost all noncentrosymmetric space groups and are independent on the electric dipole moment of molecules themselves.

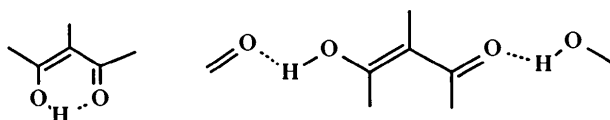
The present study involves crystallographic and theoretical research of two small aliphatic organic compounds, 4-methyl-2-oxopentanoic acid oxime, referred to hereafter as PEN (Fig. 1), and 4-oxopentanoic acid oxime (levulinic acid oxime or γ -ketovaleric acid oxime), referred to hereafter as LEV (Fig. 2).

A peculiarity of the molecules chosen is that unlike other structurally similar molecules, PEN and LEV form crystals containing cyclic arrangements of molecules bound by strong hydrogen bonds. The observed crystal structure reflects many interesting properties of isolated molecules that in turn influence the intermolecular interactions. The PEN and LEV molecules contain the oxime and carboxyl moieties placed at different relative positions. In the PEN molecule the oxime and carboxyl groups are placed sufficiently close to allow for π -electron conjugation in a way similar to β -diketones (see Gilli, Bellucci, Ferretti & Bertolasi, 1989; Bertolasi, Gilli, Ferretti & Gilli, 1991; Gilli, Bertolasi, Ferretti & Gilli, 1993). In the LEV molecule such a conjugation is not possible because the oxime and carboxyl groups are separated by a chain of two —CH₂— groups.

Gilli, Bellucci, Ferretti & Bertolasi (1989) have found that there is a remarkable correlation between the π -electron resonance and the strength of intermolecular and intramolecular hydrogen bonds formed by β -diketones. By comparison of the crystal structures of compounds containing the enol form of β -diketone moieties, the π -electron delocalization in a system of conjugated double bonds was found to lead to the strengthening of the hydrogen bonds when either an intra- or intermolecular O—H...O hydrogen bond is formed (Scheme 1).

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Similar observations in nucleic acid base pairs were referred to as π -bond cooperativity by Jeffrey & Saenger (1991). The PEN molecule can be thought of as a structural analog of enolic β -diketones where the $=\text{CH}-\text{OH}$ moiety has been replaced by the oxime $=\text{N}-\text{OH}$ moiety. Due to this structural similarity, one may expect that hydrogen bonds in PEN crystals (a possible π -conjugation) should be stronger than in LEV crystals (π -conjugation not allowed).



Scheme 1. β -diketone hydrogen bonds.

Another interesting property of compounds structurally related to PEN and LEV is worth noticing. For a long time, the complexing and extracting properties of aliphatic and aromatic hydroxyoximes were used in industrial hydrometallurgical installations to recover copper, nickel, germanium and some rare metals such as palladium, molybdenum and vanadium (Szymanowski, 1993). Hydroxyoximes form chelate complexes where the oxime and hydroxyl groups are coordinated by the metal ion while the remaining parts of the hydroxyoximes form a hydrophobic envelope around the metal. The PEN molecule contains the oxime and hydroxyl groups in a position usually found in industrially important hydroxyoximes. This structural similarity suggests that PEN may form stable chelates with transition metals. The LEV molecule contains the oxime and hydroxyl groups separated by an ethylene bridge, and in this structure the formation of chelated complexes is also possible. Due to the presence of three single C—C bonds, the LEV molecules may act as flexible bidentate ligands easily accommodating to the metal coordination sphere.

A first step in understanding the physical and chemical properties of PEN and LEV is a detailed study of their molecular structure and interactions with the environment. In the present work we performed a combined theoretical and experimental study on isolated PEN and LEV molecules. Some model systems simulating the intermolecular interactions were considered as well. An essential part of the present study is an analysis of the crystal structures formed by PEN and LEV.

Methods

X-ray structural methods have been employed to determine the crystal and molecular structures of the title compounds and *ab initio* theoretical calculations have been used to answer the questions regarding possible reasons for significant differences in the intramolecular bond distances and intermolecular hydrogen-bond dimensions in PEN and LEV structures.

Synthesis

PEN and LEV were obtained by the reaction of 4-methyl-2-oxopentanoic acid and levulinic acid (4-oxopentanoic acid), respectively, with hydroxylamine hydrochloride in alkaline solution and then purified by recrystallization. Crystals [m.p. 423–428 (PEN) and 367.2–368.1 K (LEV)] were grown from ethanol/cyclohexane solution by slow evaporation.

Crystallographic studies

Columnar colorless crystals, $0.25 \times 0.2 \times 0.5$ (PEN) and $0.15 \times 0.2 \times 0.3$ mm (LEV), were mounted on a CAD-4 single crystal diffractometer. Unit-cell parameters were obtained by the least-squares treatment of 25 reflections with $20.0 \leq 2\theta \leq 21.8^\circ$, for PEN, and with $11.2 \leq 2\theta \leq 27.2^\circ$ for LEV. Systematic absences: PEN none – space group either $P1$ or $P1$; LEV ($0k0$, k odd, $h0l$, l odd) – space group $P2_1/c$. Intensity statistics suggested in both cases centrosymmetric space groups. Intensities have been collected at 248 ± 2 K for PEN and 223 ± 2 K for LEV using graphite monochromatized $\text{Mo K}\alpha$ radiation to $2\theta \leq 50^\circ$ ($-12 \leq h \leq 12$, $-16 \leq k \leq 16$, $0 \leq l \leq 6$), for PEN, and ($-10 \leq h \leq 10$, $0 \leq k \leq 7$, $0 \leq l \leq 31$) for LEV. No significant variation in the intensities of three standard reflections was observed during data collection for PEN and LEV. 2775 (PEN) and 2348 (LEV) unique reflections (internal consistency $R_i = 0.011$ and 0.020 , respectively) have been measured using the ω - θ scan mode. 1972 and 1548 were classified as observed, respectively [$I > 1.96\sigma(I)$]. Correction for Lorentz-polarization effects but not or absorption or extinction were applied. Structures were solved using *SHELXS86* (Sheldrick, 1990). All non-H atoms were located from *E*-maps. Most of the H atoms were positioned according to the standard geometrical criteria, but the oxime and carboxyl H atoms were located from the difference Fourier maps. Structures were refined by application of *SHELXL93* (Sheldrick, 1995). Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). In the last least-squares cycles for PEN, positions and anisotropic thermal parameters for all non-H atoms, oxime and carboxyl hydrogen coordinates, and isotropic thermal parameters for ordered H atoms were refined.* The common thermal parameter for the disordered H atoms and the relative site occupancy factor for the disordered atoms were varied. In the final least-squares cycle of LEV the positions of all atoms, anisotropic thermal coefficients for non-H atoms and isotropic for the remaining H atoms, were refined. Crystal data are presented in Table 1.

* Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: AB0328). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2U, England.

Table 1. *Crystal data and refinement*

	PEN	LEV
Chemical formula	C ₆ H ₁₁ NO ₃	C ₅ H ₉ NO ₃
<i>M_r</i>	145.16	131.13
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> (Å)	10.822 (3)	8.568 (2)
<i>b</i> (Å)	13.743 (2)	5.916 (1)
<i>c</i> (Å)	5.408 (2)	26.403 (15)
α (°)	96.47 (3)	
β (°)	97.97 (3)	92.39 (1)
γ (°)	86.31 (2)	
Unit-cell volume, <i>V</i> (Å ³)	790.0 (4)	1337.2 (9)
Number of molecules (<i>Z</i>)	4	8
Calculated density, <i>D_c</i> (g cm ⁻³)	1.220	1.303
Wavelength, λ (Å)	0.71073	0.71073
Linear absorption coefficient	0.098	0.108
$[\mu(\lambda)]$ (mm ⁻¹)		
<i>F</i> (000)	312	560
Temperature, <i>T</i> (K)	248 ± 2	223 ± 2
Agreement factors <i>R</i> and <i>wR</i> ₂ *	0.0575, 0.1701	0.0387, 0.0919
Goodness of fit (<i>S</i>)	1.138	0.957
Weight (<i>w_i</i>)	1/[$\sigma^2(F_o^2)$ +(0.1129 <i>P</i>) ² +0.2035 <i>P</i>]	1/[$\sigma^2(F_o^2)$ +(0.0536 <i>P</i>) ² +0.2899 <i>P</i>]
Peaks on final $\Delta\rho$ map (e Å ⁻³)	<i>P</i> = ($F_o^2 + 2F_c^2$)/3 -0.316-0.396	<i>P</i> = ($F_o^2 + 2F_c^2$)/3 -0.172-0.215
(Shift/error) _{max}	-0.009	0.003
(Shift/error) _{av}	0.0	0.0
Number of data/number of parameters	1972/235 = 8.39	1548/235 = 6.58

* Based on *F*².

Theoretical calculations

Quantum mechanical *ab initio* calculations were used to determine the three-dimensional molecular structure and the corresponding total energies of PEN (Fig. 1) and LEV (Fig. 2). In order to better understand the molecular structure of these oximes we performed theoretical calculations for the model systems, pyruvic acid oxime (PEN-model) and acetone oxime (LEV-model). The structures of oximes bonded *via* cyclic hydrogen bonds were studied by means of the model dimeric systems pyruvic acid oxime ··· pyruvic acid oxime (PEN-model dimer, Fig. 3) and acetic acid ··· acetone oxime (LEV-model dimer, Fig. 4).

A search for the energy-optimal molecular structure has been performed in two steps. In the first step, the optimal structure was obtained with the use of the SCF/3-21G method. Next, the SCF method with a larger Gaussian basis set, *i.e.* the standard 6-31G** (6*d*) basis set, was used and the molecular structure was reoptimized. The calculations were performed with the Gaussian 90 code (Frisch *et al.*, 1990) implemented on the IBM Risk 6000 computer.

Results and discussion

PEN and LEV crystal structures consist of similar hydrogen-bonded cyclic tetramers (Fig. 5). Every tetrameric unit is built from two independent molecules, *A* and *B*, and their centrosymmetric counterparts. See-

ingly alike crystal structures differ considerably in single molecular dimensions and in intermolecular hydrogen-bond geometries.

Structure of PEN

Fig. 6 shows the *A* and *B* molecules of the PEN crystal structure. The atomic labels are marked for clarity. The final atomic parameters are given in Table 2. Table 3 contains the bond lengths and angles involving the non-H atoms. The molecules, marked as *B* in Fig. 6, are disordered in their alkyl part. The calculated C5—C4—C6 and C5'—C4'—C6' site occupancies

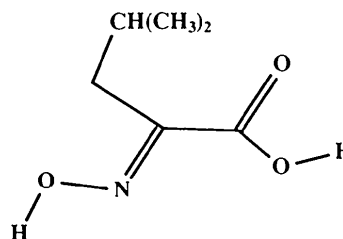


Fig. 1. 4-Methyl-2-oxopentanoic acid oxime (PEN).

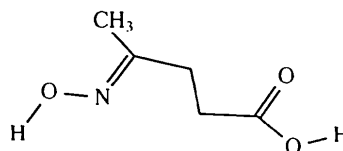


Fig. 2. Levulinic acid oxime (LEV).

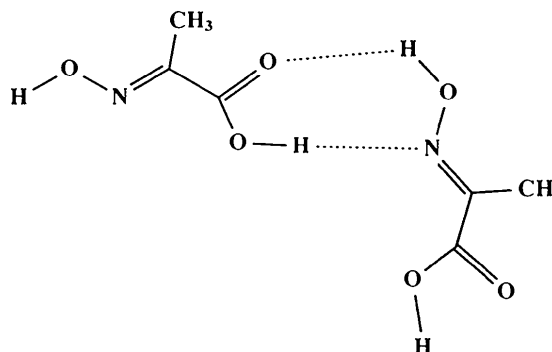


Fig. 3. PEN-model dimer.

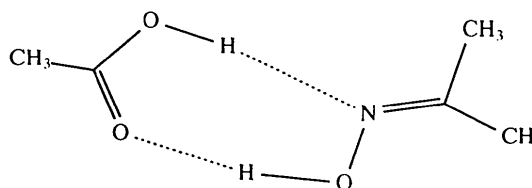


Fig. 4. LEV-model dimer.

are 0.64 and 0.36, respectively. In every PEN molecule the oxime and carboxyl groups lay almost in the same plane. The selected torsion angles are given in Table 4. The molecules are bonded by pairs of hydrogen bonds forming cyclic tetramers. Approximately planar frag-

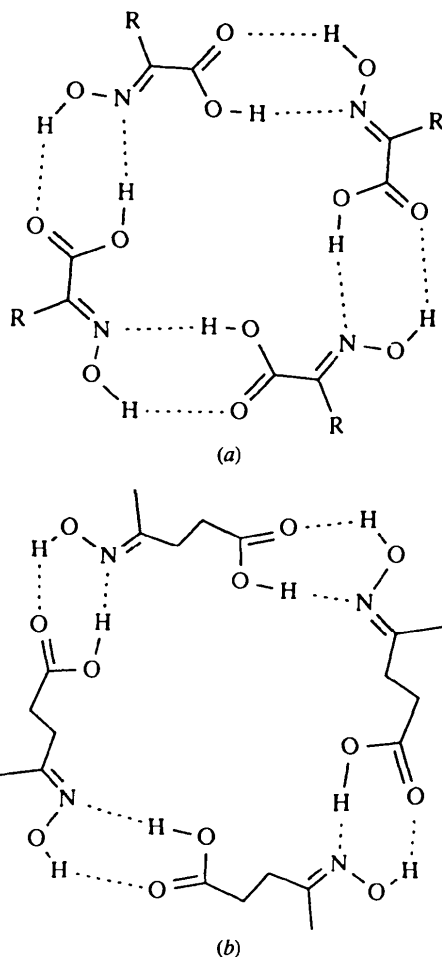


Fig. 5. Tetrameric structure of (a) PEN and (b) LEV crystals.

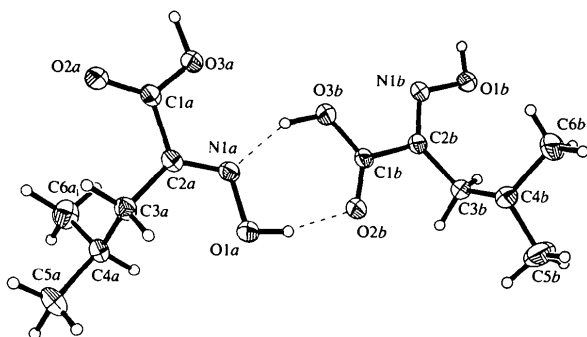


Fig. 6. The A and B molecules of the PEN crystal structure. The oxime-carboxyl hydrogen bonds are marked as dashed lines. Only one conformation of the disordered alkyl fragment of the B molecule is shown.

Table 2. Fractional atomic coordinates in the PEN structure (only the non-H atoms and the H atoms involved in hydrogen bonds are included)

	x	y	z	U_{eq} (U_{iso})
N1a	0.1453 (2)	0.6798 (2)	0.5135 (4)	0.0536 (6)
O1a	0.1563 (2)	0.7785 (2)	0.5929 (5)	0.0672 (6)
O2a	0.2498 (2)	0.4576 (2)	0.7267 (4)	0.0726 (7)
O3a	0.1327 (2)	0.49414 (15)	0.3685 (4)	0.0672 (7)
C1a	0.1983 (2)	0.5170 (2)	0.5904 (5)	0.0532 (7)
C2a	0.2083 (2)	0.6234 (2)	0.6669 (5)	0.0513 (7)
C3a	0.2875 (3)	0.6580 (2)	0.9071 (5)	0.0548 (7)
C4a	0.4154 (3)	0.6915 (2)	0.8694 (6)	0.0610 (8)
C5a	0.4845 (5)	0.7280 (4)	1.1248 (9)	0.0988 (14)
C6a	0.4934 (4)	0.6105 (3)	0.7435 (10)	0.0863 (11)
N1b	-0.1510 (2)	0.7091 (2)	-0.3453 (5)	0.0552 (6)
O1b	-0.2229 (2)	0.7315 (2)	-0.5649 (4)	0.0672 (6)
O2b	0.0067 (2)	0.83069 (15)	0.1880 (4)	0.0660 (6)
O3b	-0.0108 (2)	0.66940 (14)	0.0609 (4)	0.0610 (6)
C1b	-0.0340 (2)	0.7636 (2)	0.0353 (5)	0.0511 (7)
C2b	-0.1143 (2)	0.7859 (2)	-0.1990 (5)	0.0520 (7)
C3b	-0.1424 (3)	0.8901 (2)	-0.2500 (7)	0.0603 (8)
C4b	-0.2559 (5)	0.9321 (4)	-0.1079 (14)	0.066 (2)
C5b	-0.2596 (8)	1.0436 (5)	-0.1044 (17)	0.107 (3)
C6b	-0.3755 (5)	0.8968 (5)	-0.2589 (13)	0.086 (2)
C4b'	-0.2691 (8)	0.9346 (6)	-0.2167 (17)	0.065 (2)
C5b'	-0.2783 (12)	0.9469 (9)	0.0626 (20)	0.107 (4)
C6b'	-0.2941 (13)	1.0323 (8)	-0.3213 (24)	0.120 (4)
H10a	0.1181 (50)	0.8109 (36)	0.4853 (94)	0.123 (18)
H30a	0.1276 (35)	0.4174 (10)	0.3144 (67)	0.094 (12)
H10b	-0.2340 (39)	0.6721 (33)	-0.6402 (79)	0.097 (13)
H30b	0.0465 (34)	0.6505 (31)	0.2260 (49)	0.111 (14)

Table 3. Bond lengths (Å) and angles (°) involving non-H atoms* in the PEN structure

N1a—C2a	1.293 (4)	N1b—O1b	1.381 (3)
N1a—O1a	1.382 (3)	O2b—C1b	1.226 (3)
O2a—C1a	1.217 (3)	O3b—C1b	1.321 (3)
O3a—C1a	1.323 (3)	C1b—C2b	1.484 (4)
C1a—C2a	1.480 (4)	C2b—C3b	1.493 (4)
C2a—C3a	1.501 (4)	C3b—C4b'	1.490 (9)
C3a—C4a	1.533 (4)	C3b—C4b	1.581 (6)
C4a—C6a	1.510 (5)	C4b—C6b	1.508 (7)
C4a—C5a	1.525 (5)	C4b—C5b	1.527 (7)
N1b—C2b	1.294 (4)	C4b'—C6b'	1.508 (10)
		C4b'—C5b'	1.517 (10)
C2a—N1a—O1a	113.1 (2)	O2b—C1b—C2b	120.0 (2)
O2a—C1a—O3a	124.7 (3)	O3b—C1b—C2b	115.4 (2)
O2a—C1a—C2a	120.2 (2)	N1b—C2b—C1b	114.3 (2)
O3a—C1a—C2a	115.1 (2)	N1b—C2b—C3b	126.2 (3)
N1a—C2a—C1a	115.0 (2)	C1b—C2b—C3b	119.5 (2)
N1a—C2a—C3a	125.2 (3)	C4b'—C3b—C2b	118.2 (4)
C1a—C2a—C3a	119.8 (2)	C2b—C3b—C4b	108.3 (3)
C2a—C3a—C4a	113.7 (2)	C6b—C4b—C5b	107.5 (5)
C6a—C4a—C5a	109.6 (3)	C6b—C4b—C3b	108.8 (5)
C6a—C4a—C3a	112.5 (3)	C5b—C4b—C3b	106.8 (5)
C5a—C4a—C3a	108.7 (3)	C3b—C4b'—C6b'	112.8 (8)
C2b—N1b—O1b	113.2 (2)	C3b—C4b'—C5b'	107.3 (8)
O2b—C1b—O3b	124.6 (3)	C6b'—C4b'—C5b'	110.0 (8)

* All C—H and O—H bond lengths are in the range 0.82–1.06 Å.

ments (H10, O1, N1, C2, C1, O2, O3, H3O) of both molecules A and B are rotated roughly around the C1b—O1b direction by 1.2°. This in turn forces the H10 atoms to stay always in the plane of the molecule they are hydrogen bonded to. The same situation is observed for H3O atoms, but only in molecule A. The deviations from the respective planes are smaller than 0.04 Å.

Table 4. Selected torsion angles ($^{\circ}$) for PEN (only the H atoms involved in hydrogen bonds are included)

C2a—N1a—O1a—N1Oa	176 (4)
H1Ob*—O2a—C1a—O3a	-3 (2)
H1Ob*—O2a—C1a—C2a	178 (2)
H3Oa—O3a—C1a—O2a	0 (2)
H3Oa—O3a—C1a—C2a	179 (2)
O1a—N1a—C2a—C1a	179.4 (2)
O1a—N1a—C2a—C3a	-0.6 (4)
H3Ob—N1a—C2a—C1a	1 (2)
O2a—C1a—C2a—N1a	-176.9 (2)
O2a—C1a—C2a—C3a	3.1 (4)
O3a—C1a—C2a—N1a	4.0 (3)
O3a—C1a—C2a—C3a	-175.9 (2)
C2b—N1b—O1b—H1Ob	176 (3)
H1Ob—O2b—C1b—O3b	3 (2)
H1Oa—O2b—C1b—C2b	-176 (2)
H3Ob—O3b—C1b—O2b	0 (2)
H3Ob—O3b—C1b—C2b	180 (2)
O1b—N1b—C2b—C1b	-178.4 (2)
O1b—N1b—C2b—C3b	-0.3 (4)
H3Oa*—N1b—C2b—C1b	2 (2)
H3Oa*—N1b—C2b—C3b	-180 (2)
O2b—C1b—C2b—N1b	179.8 (2)
O2b—C1b—C2b—C3b	1.5 (4)
O3b—C1b—C2b—N1b	0.4 (3)
O3b—C1b—C2b—C3b	-177.9 (2)

* Belong to molecules related by an inversion center.

Structure of LEV

The independent *A* and *B* molecules of the levulinic acid oxime crystal structure are shown in Fig. 7. The atomic coordinates are presented in Table 5. Unlike in the PEN crystal structure, the LEV carboxyl and oxime groups do not stay in the same plane. Table 6 shows the bond lengths and bond angles involving all non-H atoms.

Crystal packing of PEN and LEV structures

Fig. 8 (PEN) and 9 (LEV) illustrate the crystal packing. Only the H atoms which are involved in hydrogen bonding were included. Hydrogen bonds are marked by dashed lines. Presented structures differ markedly from the structures presented previously (Maurin, Paul & Curtin 1992a,b 1994; Padmanabhan, Paul & Curtin, 1989) due to a different crystal packing. The crystal obtained in the present work consists of hydrogen-bonded tetramers. Previous structures corresponded to infinite chains. In oxime-carboxylic acid systems there is a preference for the formation of carboxyl-oxime hydrogen bonds rather than oxime-oxime and carboxyl-carboxyl bonds, as also shown in an acetophenone oxime-benzoic acid complex (Maurin, Winnicka-Maurin, Paul & Curtin, 1993). In the present work we found that two pairs of $N\cdots H-O$ and $O-H\cdots O$ hydrogen bonds are involved in tetramer formation. The geometry of the hydrogen bonds is listed in Table 7. We noticed that the $N\cdots H-O$ bond lengths are shorter than the corresponding bonds observed in several oxime crystal structures. We also realized that the $O-H\cdots O$ bonds are longer than typical hydrogen

Table 5. Atomic coordinates and U_{eq} in the LEV structure

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (U_{iso})
C1a	0.4702 (2)	0.2543 (4)	0.14687 (7)	0.0366 (5)
C2a	0.3709 (2)	0.4624 (4)	0.14327 (7)	0.0360 (5)
C3a	0.3132 (3)	0.5375 (4)	0.19410 (8)	0.0405 (5)
C4a	0.2156 (2)	0.7466 (3)	0.19308 (7)	0.0347 (4)
C5a	0.1533 (4)	0.8297 (5)	0.24178 (8)	0.0518 (6)
N1a	0.1884 (2)	0.8448 (3)	0.15060 (6)	0.0376 (4)
O1a	0.0948 (2)	1.0401 (2)	0.15509 (6)	0.0501 (4)
O2a	0.5067 (2)	0.1568 (2)	0.18603 (5)	0.0475 (4)
O3a	0.5167 (2)	0.1875 (3)	0.10200 (5)	0.0484 (4)
C1b	0.2068 (2)	1.0263 (3)	0.03225 (7)	0.0398 (5)
C2b	0.2549 (3)	1.0671 (4)	-0.02088 (8)	0.0430 (5)
C3b	0.1864 (3)	1.2816 (4)	-0.04374 (8)	0.0431 (5)
C4b	0.2095 (2)	1.3152 (3)	-0.09920 (7)	0.0363 (5)
C5b	0.1313 (3)	1.5113 (4)	-0.12454 (9)	0.0469 (6)
N1b	0.2952 (2)	1.1724 (3)	-0.12153 (6)	0.0382 (4)
O1b	0.3075 (2)	1.2200 (3)	-0.17362 (5)	0.0495 (4)
O2b	0.1186 (2)	1.1472 (3)	0.05472 (5)	0.0493 (4)
O3b	0.2693 (2)	0.8405 (3)	0.05223 (6)	0.0500 (4)
H1Oa	0.0876 (29)	1.0878 (46)	0.1216 (10)	0.080 (8)
H3Oa	0.5849 (33)	0.0510 (51)	0.1064 (10)	0.094 (9)
H1Ob	0.3674 (31)	1.1085 (49)	-0.1821 (10)	0.077 (9)
H3Ob	0.2425 (27)	0.8232 (41)	0.0860 (10)	0.068 (7)

Table 6. Bond lengths (\AA) and angles ($^{\circ}$) involving non-H atoms* in the LEV structure

C1a—O2a	1.213 (2)	C1b—O2b	1.213 (2)
C1a—O3a	1.326 (2)	C1b—O3b	1.323 (2)
C1a—C2a	1.497 (3)	C1b—C2b	1.498 (3)
C2a—C3a	1.516 (3)	C2b—C3b	1.513 (3)
C3a—C4a	1.493 (3)	C3b—C4b	1.499 (3)
C4a—N1a	1.276 (2)	C4b—N1b	1.279 (2)
C4a—C5a	1.496 (3)	C4b—C5b	1.485 (3)
N1a—O1a	1.414 (2)	N1b—O1b	1.412 (2)
O2a—C1a—O3a	122.9 (2)	O2b—C1b—O3b	123.0 (2)
O2a—C1a—C2a	124.8 (2)	O2b—C1b—C2b	124.3 (2)
O3a—C1a—C2a	112.3 (2)	O3b—C1b—C2b	112.6 (2)
C1a—C2a—C3a	113.0 (2)	C1b—C2b—C3b	113.0 (2)
C4a—C3a—C2a	115.5 (2)	C4b—C3b—C2b	115.9 (2)
N1a—C4a—C3a	118.3 (2)	N1b—C4b—C3b	124.4 (2)
N1a—C4a—C5a	123.2 (2)	N1b—C4b—C5b	117.7 (2)
C3a—C4a—C5a	118.5 (2)	C5b—C4b—C3b	117.9 (2)
C4a—N1a—O1a	112.43 (15)	C4b—N1b—O1b	112.7 (2)

* C—H and O—H bond lengths are in the range 0.87–1.00 \AA .

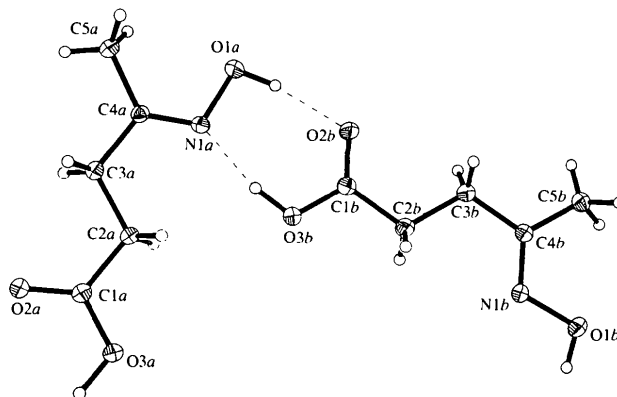


Fig. 7. The *A* and *B* molecules of the LEV crystal structure. The oxime-carboxyl hydrogen bonds are marked as dashed lines.

Table 7. Hydrogen bonds in the PEN and LEV crystals

	Distance (Å)	Angle (°)
(i) 4-Methyl-2-oxopentanoic acid oxime		
O1a—H10a...O2b	2.674 (3)	155 (5)
O1b—H10b...O2a [2565]	2.666 (3)	167 (4)
O3a—H30a...N1b [2565]	2.776 (3)	157 (3)
O3b—H30b...N1a	2.770 (3)	153 (4)
(ii) Levulinic acid oxime (4-oxopentanoic acid oxime)		
O1a—H10a...O2b	2.741 (2)	166 (2)
O1b—H10b...O2a [2665]	2.767 (2)	168 (2)
O3a—H30a...N1b [2665]	2.707 (2)	173 (2)
O3b—H30b...N1a	2.716 (3)	170 (2)

bonds in carboxylic acids dimers (Maurin, Paul & Curtin, 1992a,b, 1994, and references therein). No close contacts other than the hydrogen bonds described above were observed. No carboxyl-carboxyl or oxime-oxime interactions typical of those found in molecules containing either functional group alone were observed.

Results of calculations

The theoretically predicted bond distances in PEN and the corresponding model system PEN-model are compared with the bond distances derived from the present crystallographic structure, Table 8. Analogical data are

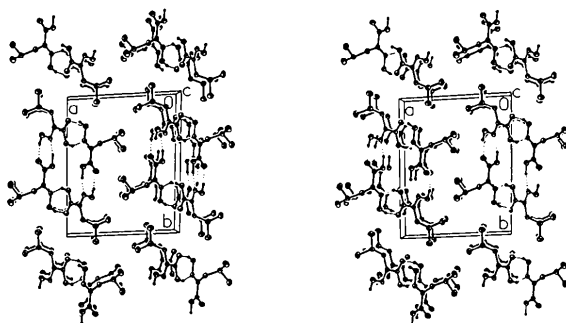


Fig. 8 Stereoview of crystal packing along the *c*-axis of PEN. Only H atoms involved in hydrogen bonds have been included. Hydrogen bonds are marked as dashed lines.

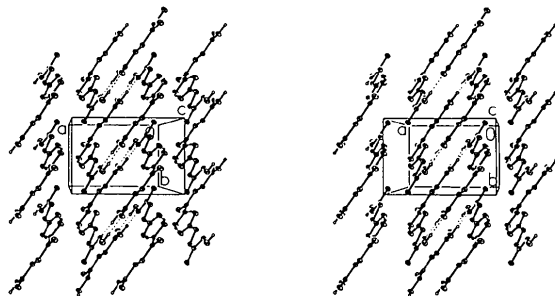
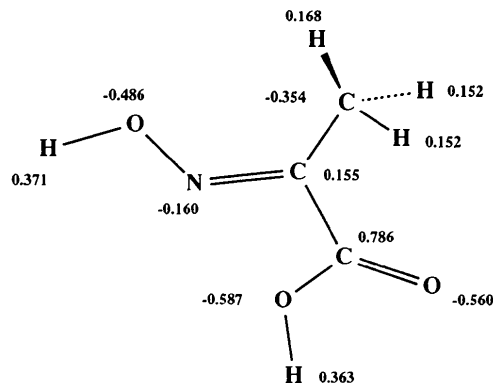


Fig. 9. Stereoview of crystal packing along the *c*-axis of LEV. Only H atoms involved in hydrogen bonds have been included. Hydrogen bonds are marked as dashed lines.

presented for LEV and for LEV-model in Table 9. The data presented in Tables 8 and 9 show that theoretically predicted bond distances agree quite well with the values derived from crystal structures

From the data presented in these tables it is also clear that the bond lengths calculated for entire oxime molecules can be adequately represented by the bond lengths obtained for model systems. The numerical values of the calculated and crystal bond distances differ slightly due to an approximate character of theoretical methodology, which does not include electron correlation effects, nuclear vibrations, or crystal field effects. Fortunately, the relative values of bond lengths are reproduced quite accurately. This observation is of primary importance for subsequent analysis of theoretical results that may help in understanding the details of the crystal structures. Particularly interesting is the region of oxime group interacting *via* hydrogen bonds with the carboxyl group of the neighboring molecule. From the crystal data it appears that the N—O bond in LEV is considerably longer (1.413 Å) than the N—O bond in PEN (1.381 Å). The intermolecular hydrogen bonds are also different in these crystals. In LEV the O—H...O bond (2.754 Å) is longer than the O—H...N bond (2.711 Å). An opposite relation is found in the PEN crystals, where the O—H...O bond (2.670 Å) is shorter than the O—H...N bond (2.773 Å). The observed differences in the structure of the oxime-carboxyl unit in LEV and PEN crystals can be explained in terms of π -resonance, which can occur in PEN molecules but it is not allowed in LEV molecules. In order to clarify the problem we can compare two structurally similar model systems: acetone oxime (LEV-model) and pyruvic acid (PEN-model). In LEV-model the oxime group is connected to two methyl groups, while in PEN-model the oxime group is connected to the single methyl group and to the carboxyl group. Due to the presence of alternating single and double bonds in PEN-model the possibility of a π -resonance between the neighboring oxime and carboxyl groups exists. Such a resonance should not occur in LEV-model. The extent of potential structure modifications originating from the π -resonance



Scheme 2. PEN-model net charges.

Table 8. Selected bond distances (in Å) for PEN and PEN-model

Bond	PEN			PEN crystal data, molecules A and B		
	SCF/3-21G	PEN-model SCF/3-21G	PEN-model SCF/6-31G**	Bond†	A	B
N—O	1.434	1.432	1.356	N1—O1	1.382 (3)	1.381 (3)
N=C	1.258	1.258	1.256	N1—C2	1.293 (4)	1.294 (4)
C _{oxime} —C _{CH₂}	1.498	1.498	1.501	C2—C3	1.501 (4)	1.493 (4)
C _{carboxyl} —C _{oxime}	1.490	1.489	1.501	C1—C2	1.480 (4)	1.484 (4)
C _{carboxyl} —O	1.345	1.344	1.320	C1—O3	1.323 (3)	1.321 (3)
C _{carboxyl} =O	1.205	1.204	1.189	C1—O2	1.217 (3)	1.226 (3)
C _{CH₂} —C _{HMe₂}	1.550	—	—	C3—C4	1.533 (4)	1.581 (6)
						1.290 (9)‡

† The numbering of the atoms corresponds to that used in Table 1 and Fig. 6.

‡ The additional entry corresponds to the second position of the disordered part of the PEN molecules (see, text)

Table 9. Selected bond distances (in Å) for LEV and LEV-model

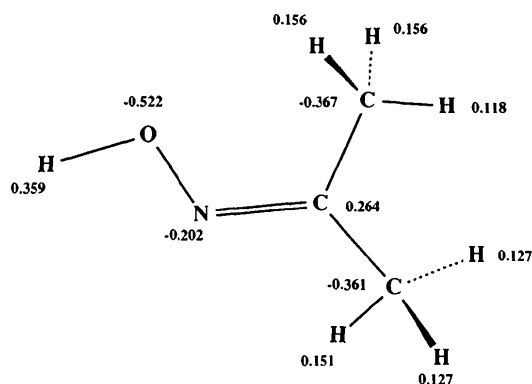
Bond	LEV			LEV crystal data, molecules A and B			
	SCF/6-31G**	LEV SCF/3-21G	LEV-model (acetone oxime) SCF/6-31G**	LEV-model (acetone oxime) SCF/3-21G	Bond†	A	B
N—O	1.377	1.450	1.378	1.453	N1—O1	1.414 (2)	1.412 (2)
N=C	1.256	1.259	1.256	1.260	N1—C4	1.276 (2)	1.279 (3)
C _{oxime} —C _{CH₂}	1.507	1.506	1.507	1.507	C4—C3	1.493 (3)	1.499 (3)
C _{carboxyl} —C _{CH₂}	1.505	1.498	—	—	C1—C2	1.497 (3)	1.498 (3)
C _{carboxyl} —O	1.330	1.356	—	—	C1—O3	1.326 (2)	1.323 (2)
C _{carboxyl} =O	1.189	1.204	—	—	C1—O2	1.213 (2)	1.213 (2)
C _{CH₂} —C _{CH₂}	1.522	1.528	—	—	C2—C3	1.516 (3)	1.513 (3)

† The numbering of the atoms correspond to that used in Table 4 and Fig. 7.

can only be estimated based on the quantum chemical calculations. The present SCF/6-31G** (6d) calculations suggest that indeed the bond length differences observed in PEN and LEV crystals can be ascribed to the π -resonance, or more strictly speaking, to the delocalization of the electron cloud on the entire PEN-model molecule. The calculated N—O bond length in LEV-model (1.378 Å) is 0.022 Å longer than the N—O bond length in PEN-model (1.356 Å). A similar value (0.032 Å) of bond contraction was observed in PEN crystals. A charge delocalization can also be seen if we compare the atomic net charges (SCF/6-31G**) in the two model systems (see Schemes 2 and 3). The sum of the net charges located on the oxime H, O and N atoms in LEV-model (−0.365 a.u.) is considerably more negative than the corresponding sum of the net charges in PEN-model (−0.275 a.u.). This suggests that the electron cloud is

Table 10. Selected bond distances (in Å) for the model of the dimeric 4-methyl-2-oxopentanoic acid oxime (pyruvic acid oxime · · pyruvic acid oxime, Fig. 3)

		SCF/3-21G	Crystal (PEN)
Pyruvic acid oxime (H—O—N= group engaged in hydrogen bond)	N—O	1.412	1.382 (3)
	N=C	1.256	1.293 (4)
	C _{oxime} —CH ₃	1.496	1.501 (4)
	H—O (oxime)	0.985	0.82 (3)
	C _{oxime} —C _{carboxyl}	1.487	1.480 (4)
	C _{carboxyl} —O	1.350	1.323 (3)
	C _{carboxyl} =O	1.201	1.217 (3)
	H—O (carboxyl)	0.968	1.064 (3)
Pyruvic acid oxime (H—O—C=O group engaged in hydrogen bond)	N—O	1.430	1.381 (3)
	N=C	1.259	1.294 (4)
	C _{oxime} —CH ₃	1.499	1.493 (3)
	H—O (oxime)	0.967	0.88 (3)
	C _{oxime} —C _{carboxyl}	1.491	1.484 (4)
	C _{carboxyl} —O	1.314	1.321 (3)
	C _{carboxyl} =O	1.221	1.226 (3)
	H—O (carboxyl)	0.988	1.061 (3)
Dimer	O · · O	2.656	2.670 (3)
	O · · N	2.809	2.772 (3)



Scheme 3. LEV-model net charges.

partly shifted towards the carboxyl group. Such a charge flow is consistent with the concept of π -resonance. By comparison of the atomic net charges located on the oxime H and N atoms one can expect the following hydrogen-bond geometry changes: when passing from LEV-model to PEN-model the H and N centers become more positive, suggesting a contraction of the O—H · · O bond and elongation of the O—H · · N bond. These qualitative predictions are supported in the present *ab initio* calculations for the model dimers (see Tables 10 and 11). The O—H · · O bond length in LEV-model dimer (2.702 Å) is 0.046 Å longer than in the

Table 11. Selected bond distances (in Å) in the model of the dimeric levulinic acid oxime (acetic acid ··· acetone oxime, Fig. 4)

	Bond	SCF/6-31G**	SCF/3-21G	Crystal (LEV)		
				A	B	
Acetone oxime (H—O—H= group engaged in hydrogen bond)	N—O	1.366	1.437	N1—O1	1.414 (2)	1.412 (2)
	N=C	1.257	1.260	N1—C4	1.276 (2)	1.279 (2)
	C _{oxime} —CH ₃	1.506	1.506	C4—C3	1.493 (3)	1.499 (3)
	H—O	0.951	0.983	H—O1	0.93 (3)	0.87 (3)
Acetic acid (H—O—C=O group engaged in hydrogen bond)	C=O	1.198	1.219	C1—O2	1.213 (2)	1.213 (2)
	C—O	1.311	1.327	C1—O3	1.326 (2)	1.323 (2)
	C—CH ₃	1.501	1.499	C1—C2	1.497 (3)	1.498 (3)
	H—O	0.964	0.998	H—O3	1.00 (3)	0.93 (2)
Dimer	O···O	2.857	2.702	O1···O2	2.754 (2)*	
	O···N	2.873	2.729	O3···N1	2.711 (2)*	

* Average values.

PEN-model dimer (2.656 Å). The O—H···N bond length (2.729 Å) in LEV-model dimer is 0.080 Å shorter than in PEN-model dimer. The corresponding bond length changes in the crystalline state are 0.084 Å for O—H···O bond contraction and 0.0682 Å for O—H···N bond elongation.

Due to several limitations of the present theoretical approach we cannot expect perfect matching of the calculated and crystal structures. The calculated bond lengths are usually overestimated and this deficiency can be removed in time- and memory-consuming calculations, which include electron correlation effects during the structure optimization. An example of the changes due to electron correlation on the calculated molecular structure can be found in a recent study by Wiberg *et al.* on malonaldehyde (Wiberg, Hadad, LePage, Breneman & Frisch, 1992; Latajka & Scheiner, 1992; Bosch, Moreno & Luch, 1992). This molecule belongs to the simplest β -diketones. The enol form of malonaldehyde is structurally related to PEN. Wiberg *et al.* (1992) have shown that in malonaldehyde the electron correlation effects significantly influence the charge distribution. The theoretically calculated density-difference maps (RHF *versus* correlated calculations) suggested that electron correlation decreases charge density within the bonding regions between the nuclei and on the nuclei themselves. An increase of the charge density in the diffuse regions around the atoms was also observed. The calculated charge-density changes are probably essential for a significant reduction of the potential barrier for proton transfer in the intramolecular O—H···O hydrogen bond. Due to differences in molecular structures one may expect that in the PEN and LEV molecules the electron correlation influences the charge distribution to a smaller extent than was found in malonaldehyde. Another shortcoming of the present approach, the influence of the crystal field, should be improved. A better representation of a crystal is obtained if more than a single molecule is included in the calculations modelling the formation of hydrogen bonds. An example of theoretical difficulties of the present approach is the prediction of the carbon-carbon C_{oxime}—C_{CH₂} and

C_{oxime}—C_{carboxyl} bond lengths in PEN oxime. In the crystalline state the C_{oxime}—C_{CH₂} and C_{oxime}—C_{carboxyl} bonds are different and this fact is interpreted in terms of different hybridization of carbon atoms, *i.e.* C(*sp*²)—C(*sp*³) for the C_{oxime}—C_{CH₂} bond and C(*sp*²)—C(*sp*²) for the C_{oxime}—C_{carboxyl} bond. From the present theoretical calculations it appears that C_{oxime}—C_{CH₂} and C_{oxime}—C_{carboxyl} bonds have identical bond lengths. Such a discrepancy between the theoretical and experimental values reflects an approximate character of the present theoretical approach.

Conclusions

The observed differences in the crystal structures of PEN and LEV originate mostly from differences in the structure of isolated molecules. Qualitatively, the structural differences can be explained in terms of the relative positions of the carboxyl and oxime groups: In PEN both groups are directly linked and in LEV they are linked *via* the —CH₂—CH₂— bridge. This in turn leads to a different charge distribution in PEN and LEV. In PEN the electronic cloud is delocalized to a larger extent than in LEV and this is reflected in the changes of the intramolecular N—O bond length and the intermolecular O—H···O and O—H···N hydrogen bonds. The theoretical calculations in the (PEN)₂ model dimer show changes in the PEN monomer molecular structure under the influence of hydrogen bonds. The calculated structural changes agree qualitatively with the phenomenon referred to as the resonance-assisted hydrogen bonding or π -bond cooperativity.

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Unusually Short Ethylene Bond and Large Amplitude Torsional Motion of (*E*)-Stilbenes in Crystals. X-ray Crystallographic Study of ‘Stiff’ Stilbenes

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Abstract

Crystal structures of (*E*)-4,4'-dimethyl-1,1'-biindanylidene, (*E*)-5,5'-dimethyl-1,1'-biindanylidene, (*E*)-6,6'-dimethyl-1,1'-biindanylidene, (*E*)-7,7'-dimethyl-1,1'-biindanylidene and (*E*)-2,2,2',2'-tetramethyl-1,1'-biindanylidene were determined by X-ray diffraction at 296 and 120 K. The observed ethylene bond length is 1.35–1.36 Å, independent of the temperature and the compound, which agrees well with the length estimated from the molecular mechanics calculations. The results make a sharp contrast with those for ordinary (*E*)-stilbenes and strongly support the interpretation that the unusual short ethylene bond in the X-ray structures of (*E*)-stilbenes is an artifact which originates from the large-amplitude torsional motion of the C—Ph bonds in crystals. The true length of the ethylene bond in (*E*)-stilbenes is safely estimated to be 1.35–1.36 Å.

Introduction

The molecular structure of (*E*)-stilbene (1) has been studied for a long time by various methods

(Waldeck, 1991; Mazzucato & Momicchioli, 1991). However, it has been a long-standing problem that the ethylene bond in the X-ray structure is unusually short (Ogawa, Sano, Yoshimura, Takeuchi & Toriumi, 1992). Since the ethylene bond is conjugated with the benzene rings, it is expected to be longer than an isolated C=C bond, whose standard bond length is 1.337 (6) Å (*International Tables for X-ray Crystallography*, 1968, Vol. III). Theoretical calculations gave the value 1.35–1.36 Å for the ethylene bond length (Warshel, 1975). The observed length remains, however, in the range 1.28–1.34 Å, which is significantly shorter than the theoretical value (Robertson & Woodward, 1937; Finder, Newton & Allinger, 1974; Bernstein, 1975; Hoekstra, Meertens & Vos, 1975; Bouwstra, Schouten & Kroon, 1984). A similar tendency is found for various compounds that have the (*E*)-stilbene skeleton (Jungk, Fronczek & Gandour, 1984; Tirado-Rives, Oliver, Fronczek & Gandour, 1984; Zobel & Ruban, 1978, 1983; Butters, Haller-Pauls & Winter, 1982; Arrieta, Domínguez, Lete, Villa & Germain, 1984; Krohn *et al.*, 1986; Bruce, Snow & Tiekink, 1987; Tirado-Rives, Fronczek & Gandour, 1985).