MOLECULAR AND CRYSTAL STRUCTURE OF BENZOHYDROXAMIC ACID AND ITS RING-SUBSTITUTED DERIVATIVES

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Received August 4, 1999
Accepted April 17, 2000

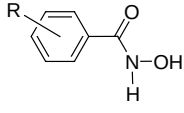
Dedicated to Professor Josef Loub on the occasion of his 70th birthday.

Crystal structure of benzohydroxamic acid and its ring-substituted derivatives $RC_6H_4C(O)NHOH$ (R = 4-Me, 4-NO_2, 4-Cl, 3-Cl and 2-Cl) was determined by single-crystal X-ray diffraction. In all the compounds, the hydroxamic group is in the planar amide form and the structures differ mainly in the tilt of the aromatic and hydroxamic acid planes. For the 2-chloro derivative, the dihedral angle of the two planes is 46.1° which corresponds to the intramolecular van der Waals contact of the *ortho*-substituents. In other compounds, the tilt originates from intermolecular hydrogen bonding and varies between 3.5 and 22.0°; four crystallographically independent molecules present in the structure of benzohydroxamic acid also differ significantly in this tilt, as well as three independent molecules of the 4-nitro derivative do. Although there are only two types of hydrogen bonding in all the compounds, a short one between OH and O–N and a second longer between NH and O=C, bonded network in the crystal is of three different types. In unsubstituted acid, its 4-Me, 4-Cl and 3-Cl derivative, the molecules are assembled into hydrogen-bonded layers stacked loosely along the largest cell parameter. As a result of the large tilt of the molecular planes in the 2-Cl compound, its molecules are linked into chains with unusual, strongly bent orientation of the aromatic groups. The self-assembly of the remaining 4-nitro compound is quite unique, consisting of pseudohexagonal, partly interpenetrating stacks. In several cases, the hydrogen bonding is supported by π-interaction of the aromatic rings.

Key words: Hydroxamic acids; Crystal structure determination; X-ray diffraction; Crystal packing; Supramolecular chemistry; H-bonds; Self assembly.

Despite the chemical and biochemical importance of hydroxamic acids[1], their structure in the solid state has been studied only very little though the literature on the molecular structure in liquids is quite extensive (for a review, see ref.[2]). In our recent work[3,4], we established that the deprotonation

site of benzohydroxamic acids and even the composition of their salts depend critically on the alkali metal ion type and on the benzene ring substituent. For instance, unsubstituted benzohydroxamic acid gives potassium or lithium acid salts by deprotonation at the N-bonded oxygen whereas, at essentially identical experimental conditions, a normal potassium salt with the N-anion is formed with the 4-nitro derivative. The salt formation is undoubtedly accompanied by changes in molecular geometry of the acid which should depend markedly on the deprotonation site. This effect, however, could not be evaluated because of the lack of crystal structure data for most of the parent acids: only 16 hits were retrieved from Cambridge Structural Database[5] for the R–C(O)NHOH fragment where R = alkyl or aryl. Therefore, we have undertaken on an X-ray single crystal structural study of these simple, mostly long-known but often incompletely characterized acids. This communication reports the crystal and molecular structures of benzohydroxamic acid (**1**) and its ring-substituted derivatives $RC_6H_4C(O)NHOH$, R = 4-Me (**2**), R = 4-NO_2 (**3**), R = 4-Cl (**4**), R = 3-Cl (**5**) and R = 2-Cl (**6**) with special attention to the self-assembly in the crystal.



	R
1	H
2	4-Me
3	4-NO_2
4	4-Cl
5	3-Cl
6	2-Cl

RESULTS AND DISCUSSION

Molecular Structures

The ORTEP drawings of the molecules with atom labelling are given in Figs 1–6. In contrast to **2** and **4**–**6** where the asymmetric part is composed of one molecule, there are four crystallographically independent molecules of **1** and three of **3**. The main difference between the individual molecules of **1** and **3** is in the conformation of the benzohydroxamate substituent relatively to the aromatic ring (see below).

The intramolecular bond distances and angles are closely similar for all the six molecules, differing from the mean of all structures by less than 3σ of the individual value. The molecular structures are also in good accordance with the average values for 20 independent fragments in 16 structures of other acids[5], including the 2 : 1 adduct of benzohydroxamic acid

with diaza-18-crown-6 ether[6] which is the only closely related structure determined by X-ray analysis. However, the hydroxamic acid groups in these fragments are frequently nonplanar, the largest displacement from the plane being usually for the oxygen of hydroxy group (as much as 0.25 Å for the hydroxamic acid derived from *N*-phthaloylglycine); the reason for this distortion is unclear. In the six structures determined in this work, the aromatic endocyclic distances and angles are unexceptional and the rings are planar within better than ±0.011 Å. The benzene rings of **2** and **4** exhibit a 50 : 50 positional disorder along their C1–C4 axes, the two positions of the benzene plane subtending the dihedral angles of 36.6(4)° for **2** and 34.9(3)°

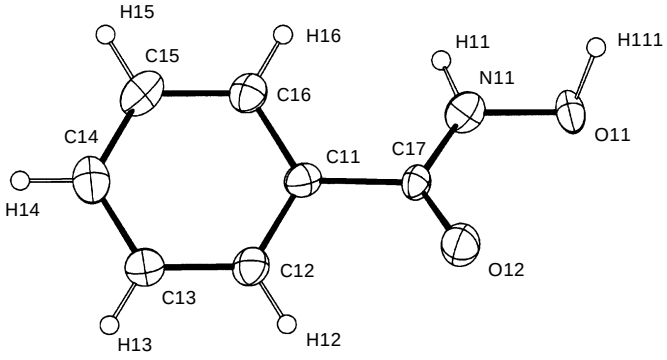


FIG. 1
View of molecule of **1** with atom labelling (ORTEP, 50% probability ellipsoids)

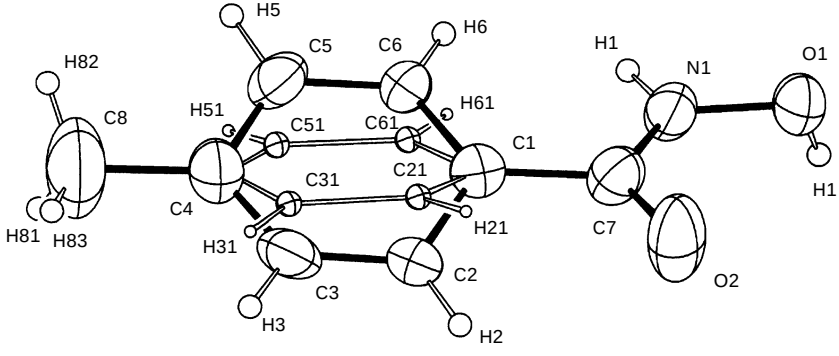


FIG. 2
View of molecule of **2** with atom labelling (ORTEP, 50% probability ellipsoids); disordered carbon atoms in second position drawn as spheres of arbitrary diameter

for **4**. Due to the disorder, metric parameters involving the disordered atoms are of lower accuracy. The displacement of the pivot atoms of the substituents from the mean aromatic planes is slight, at the most 0.089 Å for the *ortho* chlorine atom in **6**. The 2- and 3-chloro substituents are oriented *syn* to the carbonyl oxygen of the hydroxamic acid group. No remarkable differences in bond distances and angles are observed for the individual hydroxamic acid groups. Their geometry corresponds to the amide-type structure, the C(O)N(H)O moieties being planar within better than ±0.09 Å. However, the hydroxy group hydrogen is always markedly displaced from this plane, resulting in H–N–O–H torsion angles between 57 and 85°. In

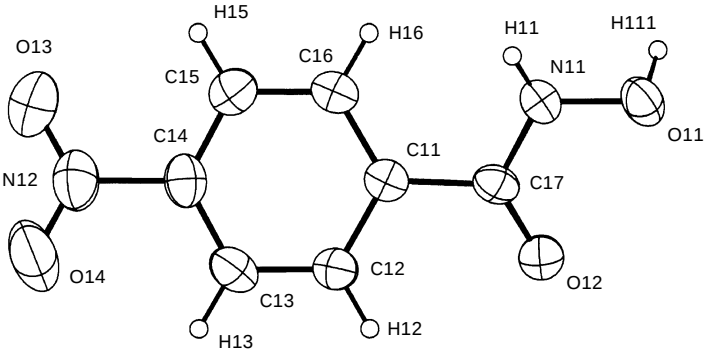


FIG. 3
View of molecule of **3** with atom labelling (ORTEP, 50% probability ellipsoids)

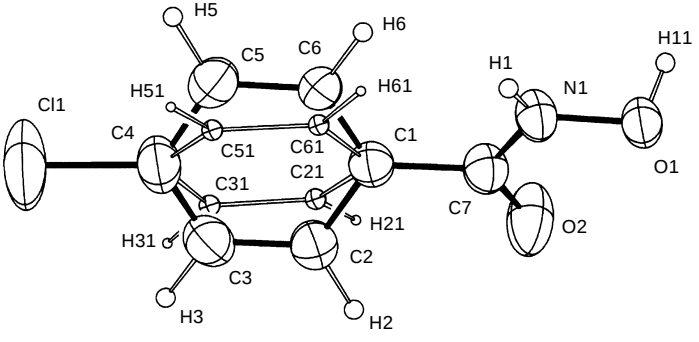


FIG. 4
View of molecule of **4** with atom labelling (ORTEP, 50% probability ellipsoids); disordered carbon atoms in second position drawn as spheres of arbitrary diameter

contrast to the bond distances and angles, there are considerable differences in the conformation of the hydroxamic acid group relatively to the benzene ring: the dihedral angles subtended by the C1–C6 and C7(O2)N1O1 planes span the range of 3.5–46.1° (Table I) for 13 independent phenyl and 11 hydroxamic acid groups in the six structures. The eleven dihedral angles of hydroxamic and *para*-substituted hydroxamic acids can be divided into three groups, five angles are within 19.8–22.2°, four

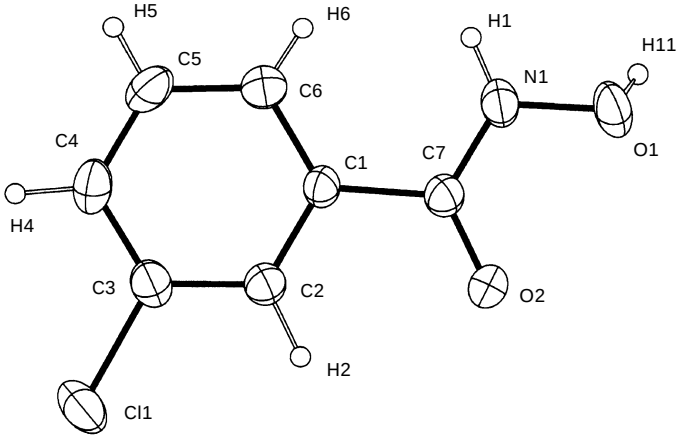


FIG. 5
View of molecule of **5** with atom labelling (ORTEP, 50% probability ellipsoids)

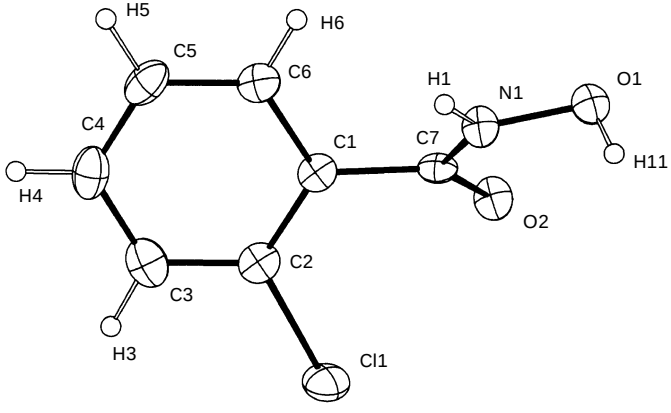


FIG. 6
View of molecule of **6** with atom labelling (ORTEP, 50% probability ellipsoids)

whithin 11.3–15.5° and two remining are 32.1 and 35.4°. Overall span of dihedral angles clearly reflects the requirements of crystal packing, however structure of population of these angles whithin their interval, especially the frequency of angle around 20°, is suggesting the preferencial molecular conformation.

Crystal Structures

In the crystal, the molecules build up supramolecular structures of various type by means of intermolecular hydrogen bonding, supported in some cases by π-stacking interaction of the aromatic rings. While the donor and acceptor atoms of the hydrogen bonds are the same in all structures and the metric parameters of the bonds are similar, the spatial orientation of the self-assembled units, the degree of the stacking interaction (if any) and the crystal morphology are strongly influenced by the substituents. There are only two kinds of hydrogen bonds: **A**, NO–H···O′=C′ and **B**, N–H···O″–N″, the metric parameters of which for 22 (11 × **A** + 11 × **B**) crystallographically independent hydrogen bonds in the six structures are in the ranges O···O′ 2.567–2.714 Å, H···O′ 1.61–1.69 Å, mean angle at H 166(9)° (type **A**) and N···O″ 2.832–2.940 Å, H···O″ 1.96–21.5 Å, mean angle at H′ 158(8)° (type **B**). As indicated by the H–N–O–H torsion angle of about 70° for all molecules, the two hydrogen bonds are approximately perpendicular in their direction, resulting mostly in layers of two-molecules thickness.

TABLE I
Dihedral angles of aromatic and hydroxamic acids planes (°)

Compound	Molecule 1	Molecule 2	Molecule 3	Molecule 4
1, R = H	21.7(2)	12.7(3)	19.8(2)	11.3(2)
2, R = 4-Me	15.1(5)	22.2(4)		
3, R = 4-NO_2	21.6(1)	35.4(1)	32.1(1)	
4, R = 4-Cl	21.9(3)	13.8(3)		
5, R = 3-Cl	3.5(3)			
6, R = 2-Cl	46.1(1)			

The conceptually simplest case of the 3-chloro derivative **5** is depicted in Fig. 7a, the alternative orientation of the same assembly in Fig. 7b demonstrates how the hydrogen bonding within the layer is supported by the π-stacking of the peripheral aromatic rings. Here the benzene rings are parallel by symmetry, the distance between their centroids being equal to the shortest cell parameter of 3.8848 Å; the rings are mutually slipped by approximately a half of their diameter (in accordance with the non-orthogonality of the crystal system), and the perpendicular distance be-

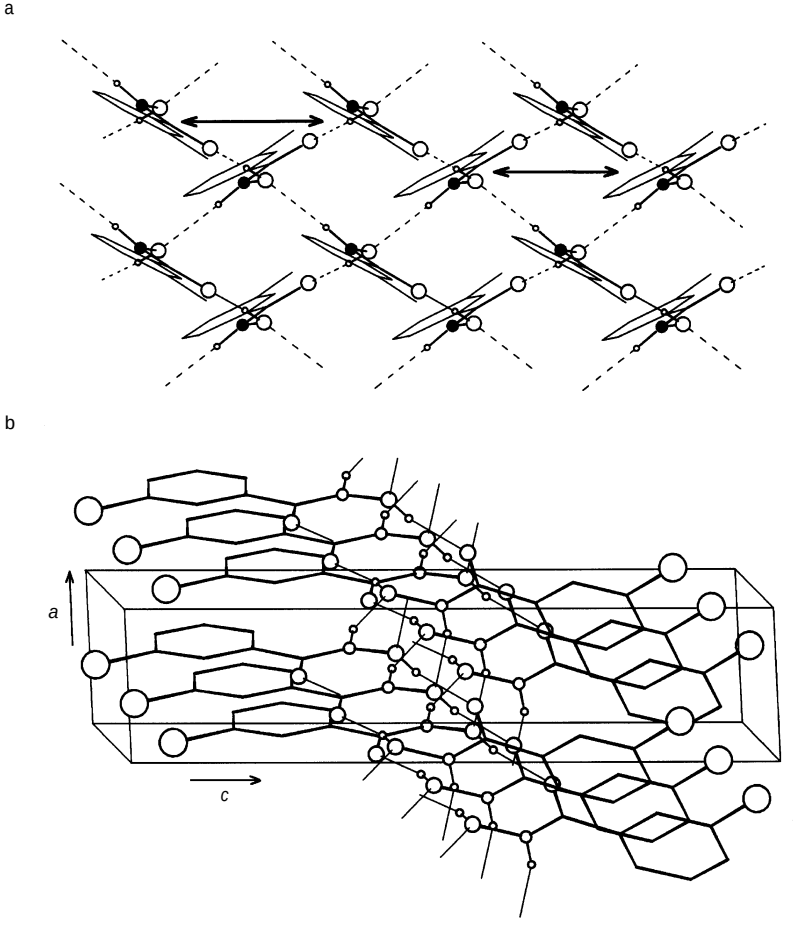


FIG. 7
Two views of crystal packing of **5** (PLUTO). Hydrogen bonds drawn as dotted lines, arrows indicate π-interaction

tween the rings is only 3.439 Å. This corresponds to the bonding π-interaction according to the usual criteria[7]. Finally, the layers are loosely packed at van der Waals distances along the third crystallographic direction. As can be expected, the preferential growth of the crystal takes place along the layers and, consequently, the material prefers the form of very thin leaflets (typically 5 × 5 × 0.01 mm), difficult to obtain as single crystals of an acceptable quality.

This layered model applies, with some variation, also to the unsubstituted acid **1**, 4-methyl derivative **2** and its 4-chloro analogue **4**. The structure of benzohydroxamic acid (**1**) is composed of four independent molecules differing mostly in the tilt of the hydroxamic acid group relatively to the benzene plane which varies between 11.3 and 22.0°. The bond distances and angles are very similar for all four molecules. Similarly to the 3-chloro derivative **5**, the molecules are self-assembled through hydrogen bonds of types **A** and **B** into layers propagating perpendicularly to the longest cell direction (Fig. 8). The four independent molecules alternate in a zig-zag manner within one layer. In contrast to **5**, the distance between the centroids of the parallel, symmetry-related benzene rings is 6.591 Å, thus precluding any π-interaction. The neighbouring layers are well separated and the crystal morphology is similar to that of **5**. However, the shortest

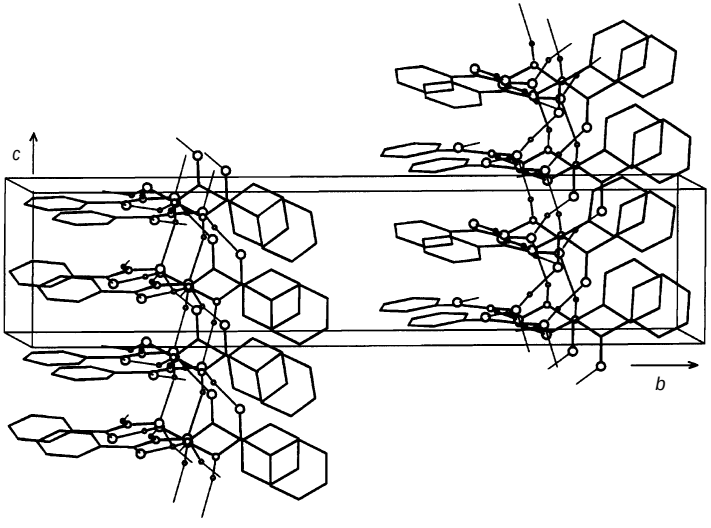


FIG. 8
Crystal packing of **1** (PLUTO)

face of the leaflets (which invariantly result from all the solvents tried, from water to xylene) has in almost all cases a stepped appearance indicating that the specimen is composed of sub-crystals due to certain mobility of the whole layers. Accordingly, the samples suffer from poor diffraction power, the selection of an acceptable crystal was a tedious procedure and the structure is the least precise within the series.

A closely related layered arrangement is adopted also by the 4-methyl derivative **2** and its chloro analogue **4**, the structures of which are very similar both at the molecular and crystal levels, despite their different crystal symmetry. Their molecular structures exhibit rotational disorder of the benzene ring along its C1–C4 axis. Consequently, the possibility of π-stacking along the appropriate cell parameter (which is sufficiently short for such an interaction) depends on the actual orientation of the neighbouring aromatic rings (Figs 9 and 10). As regards the hydrogen bonding within one layer, it is of the same type as in the previous cases. The plate-like morphology of the crystals is retained but the mobility of the layers is obviously less critical than in **1**, possibly because of blocking the layer slippage by the 4-substituent.

The last two structures do not conform to this "layered" picture for various reasons. For the 4-nitro derivative **3** it is the crystal packing which is unusual while the molecular structure appears normal. The three crystallographically independent molecules again differ mainly in the dihedral angles of the hydroxamic acid, phenyl and nitro groups, the nitro and the hydroxamic acid groups in each molecule being tilted to the benzene plane in the opposite direction. The self-assembly in the crystal is, however, quite

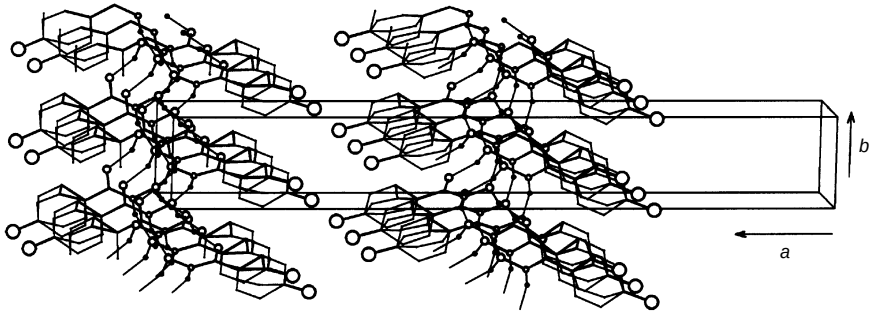


FIG. 9
Part of the unit cell content of **2** (PLUTO)

unique. Within a triclinic unit cell, two hydrogen bonds of type **A** and one of type **B**, together with their symmetry-related counterpartners, link the molecules into a cyclic hexamer of pseudohexagonal symmetry. This moiety is nonplanar but only slightly puckered. The centers of gravity of the six molecules of the hexamer lie, due to symmetry of the group, at the vertices of a planar centrosymmetric hexagon having edges of three different lengths. The hexamers are linked approximately in a perpendicular way to their average plane by means of the remaining six hydrogen bonds (two **B** and one **A** and their symmetry-related partners). This results in stacks eclipsed along the *a*-direction (Fig. 11). Clearly, the arrangement may be alternatively looked upon as six infinite chains of the **A**–**B**–**A**–**B** type, bonded side-by-side into the hexagonal stack; the first description is preferred as more illustrative regarding the unit cell content. The stack is further stabilized by six interactions between its peripheral benzene rings which are parallel due to symmetry. The perpendicular distance between them is 3.581(4) Å and the rings are mutually slipped by 42% of their diameter, which is again a π-bonding interaction. Finally, these stacks are mutually oriented in such a way that the nitro groups of the neighbouring stacks partly interpenetrate into the peripheral spaces of the parent stack and *vice versa*. This packing is very efficient, as suggested by the density of the crystals which is rather high for a compound of this composition. Clearly, the crystal morphology is totally different from that of the previous layered structures, the crystals having a needle-like to prismatic shape and display no preferential cleavage.

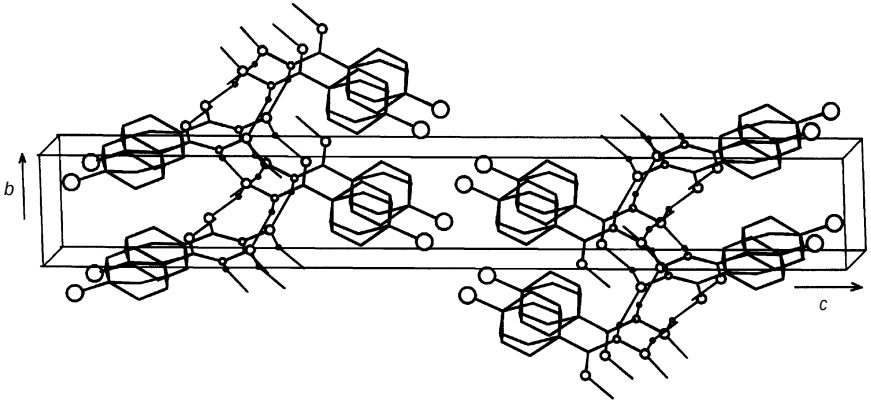


FIG. 10
Crystal packing of **4** (PLUTO)

The structure of the 2-chloro derivative **6** exhibits a major difference already at the molecular level. As a result of the strain imposed by the 2-chloro substituent, there is a remarkable tilt of the hydroxamic acid group relative to the aromatic plane by 46.1(1)°, which puts the carbonyl oxygen almost exactly into the van der Waals contact with chlorine; other molecular parameters are normal except the out-of-plane displacement of the chlorine of 0.089(2) Å due to the crowding imposed by the *ortho*-substituents. While the two kinds of the hydrogen bonds **A** and **B** remain unaltered, the large tilt of the benzene and hydroxamic acid planes prevents the molecules from being assembled into the usual layers. Instead, infinite chains of the two approximately perpendicular hydrogen bonds propagate in the *c*-direction and the peripheral benzene rings of the chain adopt an unusual, mutually strongly bent orientation (Fig. 12). The one-dimensional chain is in accordance with the crystal morphology which is needle-like with the preferential cleavage along the chain direction. For the other interaction, the distance of the centroids of the parallel benzene rings along the chain is 5.023 Å which precludes any π-interaction of sandwich structure, however there is possibility for weak contribution of

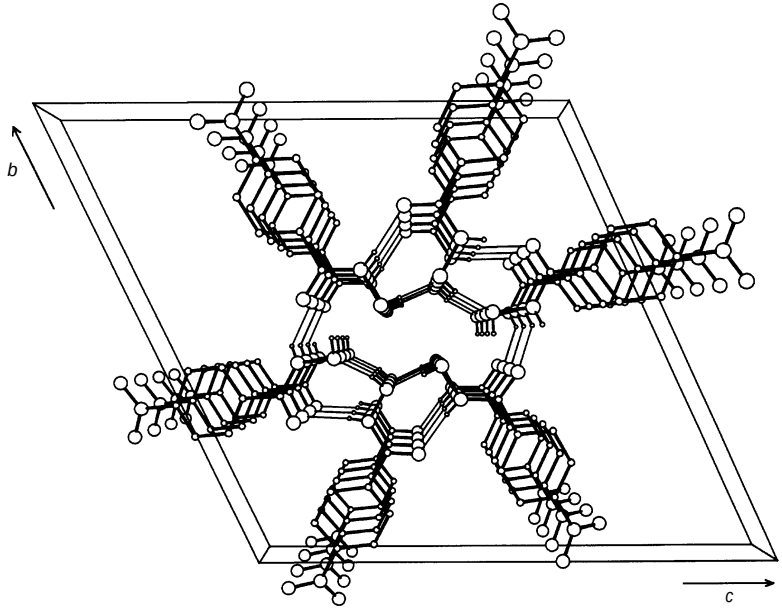


FIG. 11
Perspective view of stacking of hexamers in **3** (ORTEP, arbitrary atom sizes)

T-shape interaction in the crystal, since aromatic rings from different chains have the centroid distance 5.50 Å and dihedral angle 71.4°. Mutual orientation of rings (Fig. 13) can be regard as displaced T-shape interac-

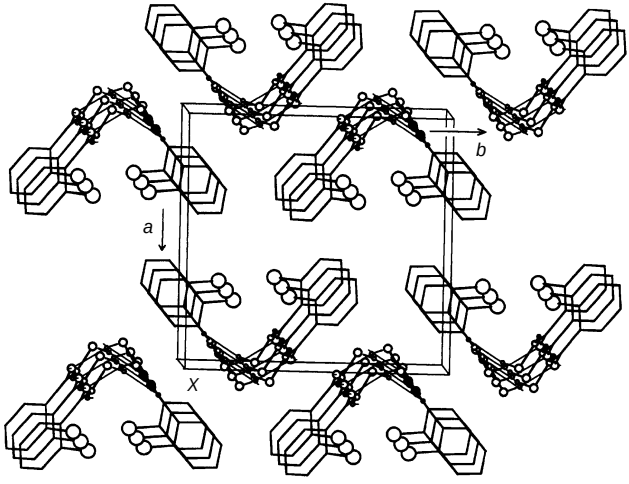


FIG. 12
Crystal packing of **6** (PLUTO)

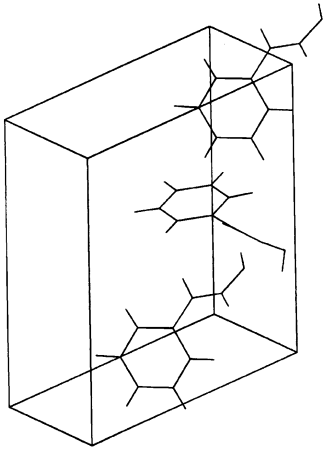


FIG. 13
Part of crystal packing of **6** (PLATON)

tion[8], but both parameters are to far from theoretic ones for minimum of interaction energie (5.00 Å and 90°), to enable unequivocal conclusion.

EXPERIMENTAL

Synthesis

4-Methylbenzohydroxamic Acid (**2**)

Compound **2** was prepared as described for benzohydroxamic acid[9] using methyl 4-methylbenzoate as the starting compound. The crude product was recrystallized twice from aqueous acetone, yield 59%, m.p. 149–150 °C (ref. 149 °C, ref.[10] 154 °C). The identity of the product was confirmed by ^{13}C NMR (DMSO-d_6): 164.4 (C=O), 130.1 (C-1), 127.0 (C-2,6), 129.0 (C-3,5), 141.1(C-4), 20.9 (CH_3).

4-Nitrobenzohydroxamic Acid (**3**)

Hydroxylamine hydrochloride (7.0 g, 0.1 mol, in 150 ml of absolute methanol) was added to a solution of 5.0 g (0.22 mol) of sodium in 150 ml of absolute methanol while shaking. The precipitated sodium chloride was filtered off, 20 g (0.11 mol) of methyl 4-nitrobenzoate was added and the solution was heated on a steam bath for 30 min. After cooling and removing some solvent under reduced pressure, the separated sodium salt was filtered off and dissolved in a minimum quantity of water. Upon acidification with acetic acid to pH 4, the light yellow compound **3** precipitated. It was recrystallized twice from hot water. The yield of 34% was low because of repeated crystallization, m.p. 186 °C (ref.[11] 165 °C, ref.[10] 186 °C). ^{13}C NMR (DMSO-d_6): 162.5 (C=O), 138.7 (C-1), 128.6 (C-2,6), 123.8 (C-3,5), 149.2 (C-4).

4-Chlorobenzohydroxamic Acid (**4**)

Preparation of compound **4** followed that of **2** with the obvious modification in the starting material. The product was recrystallized from boiling aqueous ethanol, yield 59%, m.p. 185 °C (ref.[11] 178 °C, ref.[10] 185 °C). ^{13}C NMR (DMSO-d_6): 163.3 (C=O), 131.7(C-1), 128.6 (C-2,6), 128.9 (C-3,5), 136.1 (C-4).

3-Chlorobenzohydroxamic Acid (**5**)

Preparation of compound **5** from methyl 3-chlorobenzoate also followed the procedure described above for **2**. After partial evaporation of the solvent, the precipitate was dissolved in a small amount of water and the acid separated after acidification to pH 5 with acetic acid. The crude product was recrystallized from aqueous acetone, yield 93%, m.p. 170–172 °C (ref.[12] 169–171°C). ^{13}C NMR (DMSO-d_6): 162.9 (C=O), 134.9 (C-1), 126.8 (C-2), 133.4 (C-3), 131.2 (C-4), 130.6 (C-5), 125.7 (C-6).

2-Chlorobenzohydroxamic Acid (**6**)

2-Chlorobenzoyl chloride (3.5 g, 0.02 mol) was added to anhydrous sodium carbonate (2.1 g, 0.02 mol) and hydroxylammonium chloride (1.4 g, 0.02 mol) suspended in 50 ml of diethyl ether. Subsequent addition of water (3.5 ml) produced a voluminous white precipitate of

N-hydroxy-2-chlorobenzamide (*ortho*-chlorobenzohydroxamic). The ether was distilled off and the precipitate was washed with ether and dried. The product was recrystallized from aqueous acetone, yield 28%, m.p. 152 °C (ref.[12] 158–159 °C). ^{13}C NMR (DMSO-d_6): 163.6 (C=O), 134.8 (C-1), 130.9 (C-2), 131.4.8 (C-3), 130.0 (C-4), 129.6 (C-5), 127.4 (C-6).

X-Ray Analysis

Compound **1**, $C_7H_7NO_2$, M = 137.14, monoclinic, space group $P2_1$ (No. 4), a = 6.591(4), b = 29.101(10), c = 6.624(2) Å, β = 88.55(4)°, V = 1 270(1) Å^3, Z = 8, D_c = 1.434 g/cm^3. A colourless leaflet of the dimensions 0.3 × 0.3 × 0.05 mm (from nitromethane) was measured at 150(2) K on a CAD4 diffractometer (MoKα radiation, λ = 0.71069 Å). Using the θ–2θ scan, 2 273 reflections were collected (2 238 independent R_{int} = 0.028) in the range h = –7 to 7, k = 0 to 34, l = 0 to 7 up to θ = 25°; 2 068 reflections were regarded as observed according to the $I > 2\sigma(I)$ criterion. Three standard reflections measured every hour displayed 4% intensity decrease. Absorption was neglected (μ = 0.107 mm^{-1}). The structure was solved by direct methods (SIR, ref.[13]) and refined by full-matrix least squares based on F^2 (SHELXL97, ref.[14]). The hydroxamic acid hydrogen atoms were refined isotropically, the aromatic ones were fixed in calculated positions and assigned temperature parameters 1.2 of those of their bonding partners. The reflections were corrected for pseudomeroedric twinning into orthorhombic lattice thru matrix

$$\begin{pmatrix} h' \\ k' \\ l' \end{pmatrix} = \begin{pmatrix} 0 & 0 & -1 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}$$

(The symmetry of lattice is close to orthorhombic, however R_{int} = 16.7% in the possible space group $C222_1$ is to high). The refinement for 380 parameters converged to R = 0.0794, wR = 0.2187, GOF = 1.121 and coefficient of secondary extinction of 0.019(4) for the model without twinning and to R = 0.054, wR = 0.163, GOF = 1.068 and coefficient of extiction of 0.012(4) with correction on twinning, resulting in ratio of twin's components equal to 0.205. The final difference map displayed no peaks of chemical significance. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. 119 384. Copies of the data can be obtained free of charge on request to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk) and are also available in full form by e-mail from the second author.

Compound **2**, $C_8H_9NO_2$, M = 151.16, orthorhombic, space group $Pna2_1$ (No. 33), a = 33.796(5), b = 4.7135(7), c = 4.678(1) Å, V = 745.1(2) Å^3, Z = 4, D_c = 1.347 g/cm^3. Colourless leaflet (from EtOH–xylene by slow evaporation), 0.5 × 0.4 × 0.04 mm, 293(2) K, 735 independent reflections, h = 0 to 40, k = 0 to 5, l = 0 to 5, 631 observed, 3.7% intensity decrease, μ = 0.098 mm^{-1}, 139 parameters, R = 0.0539, wR = 0.1484, GOF = 1.138, secondary extinction coefficient 0.03(1). Rotational 50 : 50 (fixed) disorder of C2, C3, C5 and C6 atoms and their hydrogens. [CCDC Registry No. 119 385]. For other details, see compound **1**.

Compound ***3***, $C_7H_6N_2O_4$, M = 182.14, triclinic, space group $P\bar{1}$ (No. 2), a = 3.742(1), b = 18.114(3), c = 18.692(2) Å, α = 114.77(1), β = 90.33(2), γ = 94.61(2)°, V = 1145.6(4) Å^3, Z = 6, D_c = 1.584, D_m = 1.59 g/cm^3 (flotation in aqueous $ZnBr_2$). The needle-like, pale yellow crystals suffered from extreme tendency to aggregation along the needle axis. After many unsuccessful attempts, one acceptable crystal of the dimensions 0.70 × 0.20 × 0.02 mm was eventually cut from a cluster grown from ethyl acetate. 3154 independent reflections mea-

sured at 293(2) K, h = 0 to 4, k = –19 to 19, l = –20 to 19, 2 282 observed, 3.2% intensity decrease, μ = 0.133 mm^{-1}, R = 0.0375, wR = 0.0929, GOF = 1.087 for 376 parameters. [CCDC Registry No. 119 386]. For other details, see compound **1**.

Compound ***4***, $C_7H_6ClNO_2$, M = 171.58, monoclinic, space group $P2_1/n$ (non-standard setting of No. 14), a = 4.7052(5), b = 4.637(1), c = 33.530(1) Å, β = 91.488(8)°, V = 731.3(2) Å^3, Z = 4, D_c = 1.558 g/cm^3. Colourless plate (from benzene–MeOH solution by slow cooling to –20 °C) solution), 0.4 × 0.4 × 0.03 mm, 1 452 measured reflections at 293(2) K, h = 0 to 5, k = 0 to 5, l = –37 to 38, 1 141 independent (R_{int} = 0.097), 937 observed, 2.5% intensity decrease, μ = 0.463 mm^{-1}, 140 parameters, R = 0.0450, wR = 0.1220, GOF = 1.083, secondary extinction coefficient 0.012(6), disorder as for **2**. [CCDC Registry No. 119 387]. For other details, see compound **1**.

Compound ***5***, $C_7H_6ClNO_2$, M = 171.58, monoclinic, space group $P2_1$ (No. 4), a = 3.8848(7), b = 5.591(1), c = 16.364(2) Å, β = 94.20(1)°, V = 354.5(1) Å^3, Z = 2, D_c = 1.608 g/cm^3. Colourless plate (vapour diffusion of pentane into solution in 1,2-dichloroethane), 0.5 × 0.5 × 0.03 mm, 1 507 measured reflections at 293(2) K, h = –4 to 4, k = 0 to 6, l = –19 to 19, 694 independent (R_{int} = 0.079), 659 observed, 6.0% intensity decrease, μ = 0.478 mm^{-1}, 124 parameters, hydrogen atoms refined isotropically, R = 0.0457, wR = 0.1073, GOF = 1.134, Flack's enantiomorph parameter –0.0(1). [CCDC Registry No. 119 388]. For other details, see compound **1**.

Compound ***6***, $C_7H_6ClNO_2$, M = 171.58, monoclinic, space group $P2_1/c$ (No. 14), a = 11.991(2), b = 12.407(2), c = 5.023(1) Å, β = 97.97(1)°, V = 740.1(2) Å^3, Z = 4, D_c = 1.540 g/cm^3. Colourless needle (from hot water by slow cooling), 0.4 × 0.07 × 0.04 mm, 1 656 reflections measured at 150(2) K, h = –13 to 13, k = 0 to 14, l = –3 to 5, 1 160 independent (R_{int} = 0.060), 945 observed, 3.2% intensity decrease, μ = 0.478 mm^{-1}, 124 parameters, hydrogen atoms refined isotropically, R = 0.0341, wR = 0.0762, GOF = 1.106. [CCDC Registry No. 119 389]. For other details, see compound **1**.

This work was supported by the Grant Agency of Czech Republic (projects No. 203/97/0242 and No. 203/99/0067) and by the Grant Agency of the Academy of Sciences of the Czech Republic (project No. A4072605).

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