Table 4. *Comparison of some* O···O *and* O···H *intermolecular contacts in acetone-type complexes of gossypol*

	GPANR	GPACT	GPTHF	GPCHN	GPBTA
O(8)—H(8O)···O(4)	2·841 (3)	2·949 (6)	3·296 (4)	3·747 (3)	3·059 (5)
H(8O)···O(4)	1·99 (4)	1·95 (6)	2·45 (4)	2·75	2·44 (7)
O(4)—H(4O)···O(7)	2·931 (5)	2·868 (7)	2·785 (4)	2·978 (8)	2·853 (5)
H(4O)···O(7)	2·89 (7)	2·83 (7)	2·77 (5)	3·00	2·34 (7)
O(5)—H(5O)···O(3)	2·751 (5)	2·777 (6)	2·762 (4)	2·795 (7)	2·948 (5)
H(5O)···O(3)	2·11 (5)	2·16 (6)	2·19 (4)	1·96	2·91 (6)

O(8) and O(2)—O(4) regions of the dimers is between O(4) and O(7) (Table 4). This contact is not a hydrogen bond due to the unfavourable orientation of the H(4O) proton involved in the intramolecular O(4)—H(4O)···O(3) hydrogen bond.

There are only van der Waals interactions between the gossypol columns constituting the host lattice. Channels parallel to [001] can be recognized. The channel is hydrophilic with the hydroxyl group O(1)—H and aldehyde oxygen O(2) located on its surface. The guests having hydrogen-bond-acceptor groups as well as those having both acceptor and donor groups could be accommodated in these channels. In GPANR, GPACT, GPTHF, GPCHN and GPBTA the guests have only hydrogen-bond-acceptor groups and a hydrogen bond between O(1)—H and the guest is formed. The guest molecule occupies the space 'over' the C(11)—C(20) naphthyl ring. In GPANR the 'best' line through acetonitrile C(1′), C(2′) and N(1′) atoms forms an angle of 52·3 (2)° with the normal to the C(11)—C(20) ring. As mentioned before, the amount of space over the ring depends on guest size and can be increased by a mutual shift of the gossypol dimers, decreasing the O(8)—H(8O)···O(4) hydrogen-bond strength.

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Solid-State Reactivity of Benzoxazinones. X-ray Structure of 2-Acetamido-5-chlorobenzoic Acid

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Abstract. $C_9H_8ClNO_3$, $M_r = 216·6$, triclinic, $P\bar{1}$, $a = 7·414\ (2)$, $b = 9·059\ (1)$, $c = 15·839\ (3)$ Å, $\alpha = 73·600\ (14)$, $\beta = 77·421\ (19)$, $\gamma = 67·786\ (18)°$, $V = 936·7$ Å^3, $Z = 4$, $D_x = 1·53$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7109$ Å, $\mu = 1·9$ cm^{-1}, $F(000) = 792$, $T = 293$ K. The structure was refined from 3198 reflections with

0108-2701/90/050813-04$03.00

Table 1. *Atomic coordinates* (× 10^4) *and equivalent isotropic thermal parameters* ($Å^2 \times 10^2$)

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

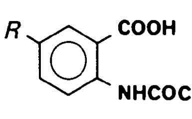
	x	y	z	U_{eq}
Cl	−1814 (1)	4581 (1)	−3792 (1)	49 (1)
C(5)	−2669 (3)	6653 (3)	−3782 (2)	33 (2)
C(4)	−3909 (4)	7193 (3)	−3066 (2)	38 (2)
C(3)	−4660 (4)	8841 (3)	−3069 (2)	36 (2)
C(2)	−4160 (3)	9964 (3)	−3799 (1)	28 (2)
C(1)	−2845 (3)	9397 (3)	−4520 (1)	28 (2)
C(6)	−2110 (3)	7730 (3)	−4498 (2)	32 (2)
C(7)	−2248 (3)	10541 (3)	−5315 (1)	32 (2)
O(1)	−1044 (3)	9790 (2)	−5925 (1)	47 (2)
O(2)	−2806 (3)	12009 (2)	−5407 (1)	49 (2)
N	−4930 (3)	11658 (2)	−3844 (1)	36 (2)
C(8)	−6419 (4)	12520 (3)	−3323 (2)	34 (2)
O(3)	−7312 (3)	11878 (2)	−2673 (1)	56 (2)
C(9)	−6898 (6)	14340 (4)	−3606 (3)	49 (4)
Cl′	5363 (1)	−8448 (1)	463 (1)	42 (1)
C(5′)	3818 (3)	−6518 (2)	17 (2)	29 (2)
C(4′)	3807 (3)	−6000 (3)	−888 (2)	34 (2)
C(3′)	2591 (3)	−4457 (3)	−1251 (2)	32 (2)
C(2′)	1376 (3)	−3407 (2)	−707 (1)	25 (2)
C(1′)	1377 (3)	−3941 (2)	217 (1)	24 (2)
C(6′)	2607 (3)	−5508 (2)	568 (1)	26 (2)
C(7′)	84 (3)	−2899 (2)	839 (1)	27 (2)
O(1′)	162 (3)	−3645 (2)	1681 (1)	40 (2)
O(2′)	−964 (3)	−1498 (2)	611 (1)	47 (2)
N′	112 (3)	−1836 (2)	−1048 (1)	30 (2)
C(8′)	−210 (3)	−1100 (3)	−1893 (1)	31 (2)
C(9′)	−1719 (5)	589 (3)	−2016 (2)	42 (3)
O(3′)	617 (3)	−1735 (2)	−2522 (1)	52 (2)

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

Cl—C(5)	1·742 (2)	Cl′—C(5′)	1·733 (2)
C(5)—C(4)	1·374 (3)	C(5′)—C(4′)	1·377 (3)
C(5)—C(6)	1·374 (3)	C(5′)—C(6′)	1·375 (3)
C(4)—C(3)	1·380 (4)	C(4′)—C(3′)	1·383 (3)
C(3)—C(2)	1·395 (3)	C(3′)—C(2′)	1·391 (3)
C(2)—C(1)	1·409 (3)	C(2′)—C(1′)	1·405 (3)
C(2)—N	1·406 (3)	C(2′)—N′	1·403 (3)
C(1)—C(6)	1·390 (3)	C(1′)—C(6′)	1·396 (3)
C(1)—C(7)	1·491 (3)	C(1′)—C(7′)	1·486 (3)
C(7)—O(1)	1·315 (3)	C(7′)—O(1′)	1·315 (3)
C(7)—O(2)	1·209 (3)	C(7′)—O(2′)	1·208 (2)
N—C(8)	1·349 (3)	N′—C(8′)	1·345 (3)
C(8)—O(3)	1·222 (3)	C(8′)—O(3′)	1·221 (3)
C(8)—C(9)	1·501 (4)	C(8′)—C(9′)	1·502 (4)
Cl—C(5)—C(4)	119·8 (2)	Cl′—C(5′)—C(4′)	120·0 (2)
Cl—C(5)—C(6)	119·3 (2)	Cl′—C(5′)—C(6′)	119·8 (2)
C(4)—C(5)—C(6)	120·9 (2)	C(4′)—C(5′)—C(6′)	120·2 (2)
C(5)—C(4)—C(3)	120·2 (2)	C(5′)—C(4′)—C(3′)	120·4 (2)
C(4)—C(3)—C(2)	120·1 (2)	C(4′)—C(3′)—C(2′)	120·4 (2)
C(3)—C(2)—C(1)	119·4 (2)	C(3′)—C(2′)—C(1′)	119·2 (2)
C(3)—C(2)—N	122·2 (2)	C(3′)—C(2′)—N′	122·2 (2)
C(1)—C(2)—N	118·4 (2)	C(1′)—C(2′)—N′	118·6 (2)
C(2)—C(1)—C(6)	119·3 (2)	C(2′)—C(1′)—C(6′)	119·4 (2)
C(2)—C(1)—C(7)	121·7 (2)	C(2′)—C(1′)—C(7′)	122·1 (2)
C(6)—C(1)—C(7)	119·0 (2)	C(6′)—C(1′)—C(7′)	118·5 (2)
C(5)—C(6)—C(1)	120·2 (2)	C(5′)—C(6′)—C(1′)	120·5 (2)
C(1)—C(7)—O(1)	112·9 (2)	C(1′)—C(7′)—O(1′)	113·8 (2)
C(1)—C(7)—O(2)	124·7 (2)	C(1′)—C(7′)—O(2′)	124·3 (2)
O(1)—C(7)—O(2)	122·4 (2)	O(1′)—C(7′)—O(2′)	121·9 (2)
C(2)—N—C(8)	129·8 (2)	C(2′)—N′—C(8′)	129·2 (2)
N—C(8)—O(3)	123·0 (2)	N′—C(8′)—O(3′)	123·8 (2)
N—C(8)—C(9)	114·6 (2)	N′—C(8′)—C(9′)	114·9 (2)
O(3)—C(8)—C(9)	122·4 (3)	O(3′)—C(9′)—C(8′)	121·3 (2)

$I > 3\sigma(I)$ to $R = 0{\cdot}037$. The two independent molecules have almost the same planar conformation. The maximum deviation from the least-squares plane is 0·52 Å for atom O(2′). All H atoms were found on a difference map. The intermolecular hydrogen-bond distance between O(1) and O(3′) at position 2/010 is 2·62 Å.

Introduction. *N*-Acetylanthranilic acid (2-acetamidobenzoic acid) (I) (R = H) and related molecules have been reported as products of solid–gas hydrolysis of benzoxazinones (Etter, Errede & Vicens, 1981; Vicens, Decoret, Royer & Etter, 1985; Vicens, Decoret, Gaget, Etter & Errede, 1983) and naphthoxazinones (Etter, 1982).



(I) R = H , Cl

Anisotropic behavior of reaction propagation in the crystalline structure has been explained by the arrangement of molecules in the starting crystals. Similarly, molecules related to (I) have been proposed as starting material for cyclodehydration in the solid state (Shklover & Timofeeva, 1985). Also, (I) (R = H) has been reported to be a strongly triboluminescent material related to its polar noncentrosymmetric space group (Mascarenhas, de Almeida & Lechat, 1980). The crystal-structure determination of the title compound (I) (R = Cl) was undertaken to provide necessary information abouts its use as the starting material for cyclodehydration and its occurrence as the final product of benzoxazinone hydrolysis in the solid state.

The presence of a Cl atom at position C(5) is due to the well known steering ability of a chloro group when substituted on an aromatic moiety to direct the packing mode of molecules in the crystal (Nalini & Desiraju, 1986). *N*-Acetyl-5-chloroanthranilic acid (I) (R = Cl) was obtained by refluxing 2-amino-5-chlorobenzoic acid and acetic anhydride with subsequent hydrolysis of the solid material with water vapor.

Experimental. Colorless plate-like crystal 0·21 × 0·42 × 0·27 mm, CAD-4 four-circle diffractometer, room temperature, Mo $K\alpha$ radiation, lattice parameters from 25 reflections ($20 < \theta < 30°$); 5901 intensities with $(\sin\theta)/\lambda < 0{\cdot}703$ Å^{-1} in the ω–2θ scan (width of the scan fixed at 2·1° and $-10 < h < 10$, $-12 < k < 12$, $l < 22$), from which 3198 with $I > 3\sigma(I)$ used for structure refinement. Three standard reflections, no intensity variation.

Lp correction applied, absorption and extinction ignored; *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and Fourier methods, anisotropic full-matrix on F (Sheldrick, 1976), H from $\Delta\rho$ synthesis, isotropically refined; atomic scattering factors from *International Tables for X-ray Crystallography* (1974), for H from Stewart, Davidson & Simpson (1965); final $R = 0{\cdot}037$, unit weight; $\Delta\rho$ in final map $= 0{\cdot}24$, $-0{\cdot}22$ e Å^{-3}, $(\Delta/\sigma)_{\max} = 0{\cdot}005$ for the scale factor.

Discussion. Fractional coordinates and equivalent isotropic thermal parameters for non-H atoms are given in Table 1, selected interatomic distances and angles in Table 2.* The conformation of the molecule and the atomic numbering are depicted in Fig. 1. Crystal packing is shown in Fig. 2.

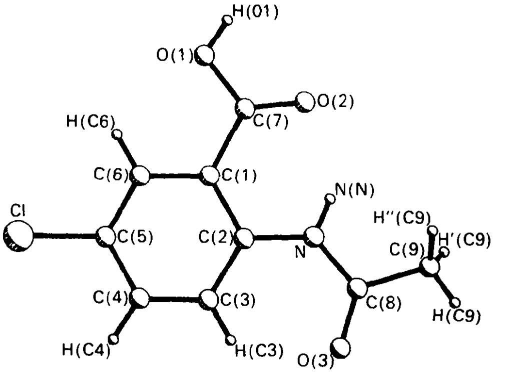


Fig. 1. Molecular drawing indicating labeling of atoms of molecule (1). A prime has been used for the numbering of the atoms of the second molecule.

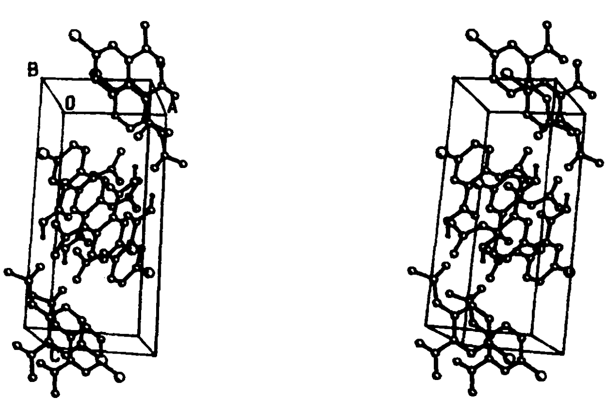


Fig. 2. Stereoview of the structure for one orientation.

There are no significant differences between the bond lengths and bond angles in the two independent molecules (1, 1′). The two molecules are almost planar with more deviation for molecule (1): O(3) is 0·52 Å above the mean plane containing the benzene ring, against 0·13 Å for O(2′).

If *P*1 is the plane containing the Cl atom and the benzene ring, *P*2 the plane through N, C(8), O(3) and C(9) and *P*3 the plane containing C(7), O(1) and O(2), the greatest differences between the dihedral angles for the two independent molecules and the results of Mascarenhas *et al.* (1980) concern the angle between *P*1 and *P*2 where the values are 11·1, 2·8 and 7·3°, respectively. The angles between *P*1 and *P*3 (1·9, 5·2, 4·9°) and *P*2 and *P*3 (11·1, 7·9, 6·6°) are less scattered.

No intermolecular distances between the two independent molecules are less than the sum of the van der Waals radii of the atoms involved; molecules (1) and (1′) are separated by distances of the order of 4·0 Å, Cl—C(6) = 3·91 Å.

A hydrogen bond [O(1)···O(3′) = 2·62 Å with H(O11)—O(23) = 1·79 Å] links atom O(1) of molecule (1) to atom O(3′) of molecule (1′) shifted by one **b** translation.

The role of hydrogen-bond patterns in influencing the packing of carboxylic acids and amides has been reported previously (Etter, 1982; Taylor & Kennard, 1982).

From the X-ray crystal structure of (I) (R = Cl) it appears that hydrogen bonds direct the arrangement of molecules in the crystal despite the presence of the chloro group. These hydrogen bonds are thus involved in the mode of reaction of crystals of (I) (R = Cl) in cyclodehydration and in the phase formation of products during gaseous hydrolysis of parent crystalline benzoxazinones (Shklover & Timofeeva, 1985). Work is in progress in these two directions.

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, mean planes and dihedral angles between planes and shortest intermolecular distances between non-H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52507 (40 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structures of Two Isomeric Hydroxamic Acids: *N*-Methyl-*p*-toluohydroxamic Acid (MTH) and *N*-(4-Methylphenyl)acetohydroxamic Acid (MPA)

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Abstract. MTH, $C_9H_{11}NO_2$, $M_r = 165{\cdot}19$, monoclinic, $P2_1/n$, $a = 7{\cdot}106\,(2)$, $b = 10{\cdot}211\,(3)$, $c = 11{\cdot}962\,(2)$ Å, $\beta = 97{\cdot}99\,(2)^\circ$, $V = 859{\cdot}5$ Å^3, $Z = 4$, $D_x = 1{\cdot}276$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}054$ mm^{-1}, $F(000) = 352$, $T = 138$ K, final $R = 0{\cdot}042$ for 1687 reflections with $I \geq 2\sigma(I)$. MPA, $C_9H_{11}NO_2$, $M_r = 165{\cdot}19$, orthorhombic, $Pbca$, $a = 9{\cdot}300\,(3)$, $b = 9{\cdot}463\,(4)$, $c = 19{\cdot}340\,(6)$ Å, $V = 1702{\cdot}0$ Å^3, $Z = 8$, $D_x = 1{\cdot}29$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, $\mu = 0{\cdot}665$ mm^{-1}, $F(000) = 704$, $T = 138$ K, final $R = 0{\cdot}044$ for 1362 reflections with $I \geq 3\sigma(I)$. The hydroxamate group in each compound assumes the *trans* conformation as observed in other secondary hydroxamic acids. The interchange of the C and N substituents influences the planarity and dimensions (C=O, C—N bonds) of the hydroxamate moiety. In MTH the hydroxamate group shows significant deviation from planarity; the r.m.s. deviation of the four atoms, O=C—N—O(H), is 0·094 Å, whereas in MPA it is only 0·004 Å. This nonplanarity is due largely to out-of-plane bending at N, $\chi_N = 23{\cdot}9\,(1)^\circ$, as compared to $\chi_N = 0{\cdot}1^\circ$ for MPA. The phenyl ring in MPA is nearly coplanar with the hydroxamate plane (dihedral angle of 10·3°), but is significantly rotated from the hydroxamate plane in MTH (dihedral angle of 43·8°). Electronic differences in the two molecules are considered.

Introduction. Hydroxamic acids constitute an interesting class of weak organic acids ($pK_a \simeq 8{\cdot}3$) of the general chemical form R_1—C(O)—N(OH)—R_2, which have a wide range of chemical and biochemical applications (see Kehl, 1982; Agarwal, 1980; Chatterjee, 1978). Perhaps the most important property of these compounds as unsymmetrical bidentate ligands is their ability to form thermodynamically stable chelates with spherically symmetric trivalent transition metals; they exhibit unusually high specificity for Fe^{3+} (and Al^{3+}, Ga^{3+}) over other biologically important metal ions (which are generally divalent). As a consequence of this latter property, a large number of naturally occurring iron(III) chelating agents of procaryotic and eucaryotic origin (siderophores) utilize hydroxamate functional groups for ferric ion coordination (Hider, 1984). The specificity and high stability of these complexes is dependent on the geometric and electronic arrangements of the ligating O atoms in the five-membered ferric–hydroxamate chelate ring, which in turn can be influenced markedly by inductive and resonance effects introduced into the ligand and chelate by the carbon (R_1) and nitrogen (R_2) substituents of the hydroxamate functionality (Monzyk & Crumbliss, 1979; Brink & Crumbliss, 1984).

There has been considerable interest in the design for clinical use of synthetic secondary hydroxamic acids ($R_2 \neq$ H) with simpler stereochemistry than that possessed by siderophores. A series of substituted *N*-phenylacetohydroxamic and *N*-methylbenzohydroxamic acids has been synthesized and studied to determine the effect of electron-releasing and withdrawing substituents on the acidity of the ligand, and the kinetic and thermodynamic stability of their (monohydroxamato)iron(III) complexes (Monzyk & Crumbliss, 1979, 1980; Brink & Crumbliss, 1984; Brink, Fish & Crumbliss, 1985). In our continuing study of the molecular structures of iron-chelating agents (siderophores) and their metal chelates, we have previously reported the structures of several of these secondary hydroxamic acids (Mocherla, Powell, Barnes & van der Helm, 1983; Mocharla, Powell & van der Helm, 1984; Powell & van der Helm, 1987). We present here the structures

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