STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
TAYLOR, R. & KENNARD, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.
VICENS, J., DECORET, C., GAGET, C., ETTER, M. C. & ERREDE, L. A. (1983). *Mol. Cryst. Liq. Cryst.* **96**, 39–44.
VICENS, J., DECORET, C., ROYER, J. & ETTER, M. C. (1985). *Isr. J. Chem.* **25**, 306–311.

Acta Cryst. (1990). C**46**, 816–821

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

BY ANDREAS DIETRICH, DOUGLAS R. POWELL, D. L. ENG-WILMOT, M. B. HOSSAIN AND DICK VAN DER HELM

Department of Chemistry, University of Oklahoma, Norman, OK 73019, *USA*

(*Received* 28 *November* 1988; *accepted* 21 *July* 1989)

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, $\beta = 97{\cdot}99\ (2)°$, $V = 859{\cdot}5$ 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, $\chi_N = 23{\cdot}9\ (1)°$, as compared to $\chi_N = 0{\cdot}1°$ 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

0108-2701/90/050816-06$03.00

of two isomeric secondary hydroxamic acids, *N*-methyl-*p*-toluohydroxamic acid (MTH) and *N*-(4-methylphenyl)acetohydroxamic acid (MPA), where $R_1(C_6H_4CH_3)$ and $R_2(CH_3)$ are interchanged. The results of these structures are compared with those observed in some other related hydroxamic acids. The structure of MTH has been determined earlier (Kalinin, Antipin, Yurchenko & Struchkow, 1982).

Experimental. MTH was synthesized using the Schotten–Baumann reaction (Gupta & Tandon, 1969) by the slow dropwise addition of 0·1 mol of 4-methylbenzoyl chloride in diethyl ether to a solution of *N*-methylhydroxylamine (0·1 mol) in diethyl ether containing 0·15 mol $NaHCO_3$, at 196 K. Yield 42%; m.p. 387–388 K. Colorless crystals were grown from an ethyl acetate solution equilibrated with benzene at 277 K; 0·60 × 0·50 × 0·20 mm; space group from systematic absences ($h0l$ when $h+l$ is odd; $0k0$ when k is odd); CAD-4 single-crystal X-ray diffractometer with a low-temperature device, Mo $K\bar{\alpha}$ radiation with graphite monochromator, lattice parameters from setting of 48 reflections with $14 < \theta < 23°$ [λ(Mo $K\alpha_1$) = 0·70926 Å]. 3782 reflections with $2\theta \le 53°$; 1780 unique after merging (R_{int} = 0·023), $0 \le h \le 9$, $0 \le k \le 12$, $-15 \le l \le 15$; θ–2θ scan, variable scan width $(0{\cdot}80 + 0{\cdot}20\tan\theta)°$; three standard reflections measured every 7200 s of X-ray exposure, maximum variation 3·5%; intensities scaled for monitor variation; 1687 observed reflections on the basis $I \ge 2\sigma(I)$; Lorentz and polarization corrections, no absorption correction. Structure solved by direct methods using *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980) and refined by the full-matrix least-squares routine *SHELX*76 (Sheldrick, 1976). All the H atoms from the ΔF map were refined isotropically; anisotropic refinement of all non-H atoms; $\sum w(|F_o| - |F_c|)^2$ was minimized, where $w = 1/\sigma^2(F)$; final R = 0·044 for all 1780 data, R = 0·042, wR = 0·060 for 1687 observed reflections; $(\Delta/\sigma)_{max}$ = 0·031, S = 2·4; highest peak in the final difference map 0·26 e Å^{-3} near the C(7) methyl group.

MPA, obtained as a gift from Dr A. L. Crumbliss, Duke University, gave colorless, rod-shaped crystals grown by diffusing cyclohexane into an ethyl acetate solution; 0·45 × 0·12 × 0·10 mm; space group from systematic absences ($0kl$ when $k = 2n+1$; $h0l$ when $l = 2n+1$ and $hk0$ when $h = 2n+1$) and intensity statistics; cell parameters from 48 reflections with $21 < \theta < 25°$ [λ(Cu $K\alpha_1$) = 1·54051 Å], all unique data with $2\theta \le 150°$, $0 \le h \le 11$, $0 \le k \le 11$, $0 \le l \le 24$; θ–2θ scan with scan width $(0{\cdot}75 + 0{\cdot}20\tan\theta)°$, 1742 total unique reflections, 1362 observed on the basis of $I \ge 3\sigma(I)$, seven observed reflections with $\chi \sim 90°$ and $2\theta > 130°$ had unreasonable background due to scattering from the goniometer head and were omitted; three monitor reflections showed maximum variation of 2·5%; structure solved by the direct-methods program as in *SHELX*76 (Sheldrick, 1976); refined by full-matrix least squares minimizing $\sum w(|F_o| - |F_c|)^2$; H atoms located from the difference electron density maps; O, N, C atoms refined anisotropically; H atoms refined isotropically; final R = 0·063 for all data, R = 0·044, wR = 0·056; S = 1·81; $w = 1/\sigma^2(F)$; $(\Delta/\sigma)_{max}$ = 0·043, largest peak in the final difference map is 0·19 e Å^{-3}.

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for the non-*H *atoms with e.s.d.'s for the last digit in parentheses*

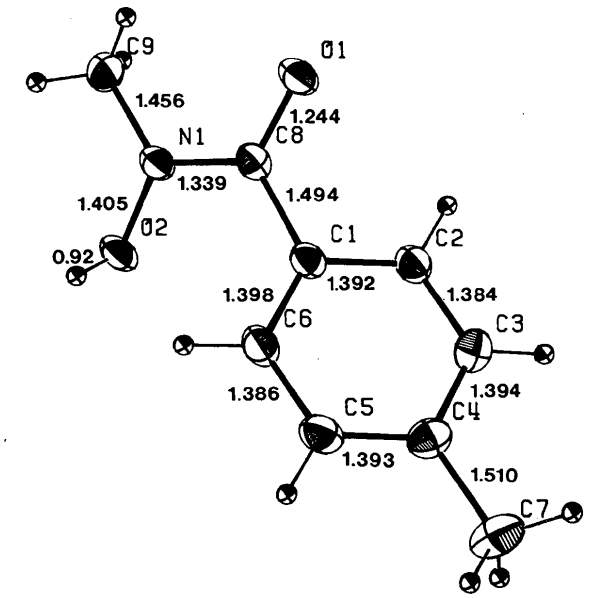
$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq} (Å^2)
MTH				
C(1)	1·0146 (2)	0·7417 (1)	0·2271 (1)	0·0232 (4)
C(2)	0·8949 (2)	0·8496 (1)	0·2270 (1)	0·0260 (4)
C(3)	0·7144 (2)	0·8484 (1)	0·1661 (1)	0·0295 (4)
C(4)	0·6489 (2)	0·7394 (1)	0·1020 (1)	0·0289 (4)
C(5)	0·7707 (2)	0·6327 (1)	0·1009 (1)	0·0299 (4)
C(6)	0·9511 (2)	0·6323 (1)	0·1623 (1)	0·0278 (4)
C(7)	0·4524 (2)	0·7390 (2)	0·0350 (1)	0·0419 (5)
C(8)	1·2117 (2)	0·7558 (1)	0·2882 (1)	0·0233 (4)
C(9)	1·4923 (1)	0·6634 (1)	0·4041 (1)	0·0306 (4)
N(1)	1·3039 (1)	0·6529 (1)	0·33906 (9)	0·0252 (3)
O(1)	1·2945 (1)	0·86327 (9)	0·28958 (8)	0·0324 (3)
O(2)	1·1989 (1)	0·54435 (8)	0·36760 (8)	0·0285 (3)
MPA				
C(1)	0·6295 (2)	0·9315 (2)	0·5867 (1)	0·0251 (9)
C(2)	0·5306 (2)	0·8951 (2)	0·6379 (1)	0·0287 (10)
C(3)	0·5467 (2)	0·9480 (2)	0·7044 (1)	0·0317 (10)
C(4)	0·6574 (2)	1·0408 (2)	0·7219 (1)	0·0323 (10)
C(5)	0·7505 (2)	1·0797 (2)	0·6694 (1)	0·0349 (11)
C(6)	0·7389 (2)	1·0268 (2)	0·6028 (1)	0·0318 (10)
C(7)	0·6764 (3)	1·0938 (3)	0·7948 (1)	0·0428 (14)
C(8)	0·5396 (2)	0·7682 (2)	0·4941 (1)	0·0276 (9)
C(9)	0·5605 (3)	0·7263 (2)	0·4197 (1)	0·0343 (11)
N(1)	0·6223 (2)	0·8755 (2)	0·5182 (1)	0·0255 (8)
O(1)	0·4550 (2)	0·7050 (1)	0·5327 (1)	0·0329 (7)
O(2)	0·7129 (2)	0·9410 (1)	0·4701 (1)	0·0309 (7)

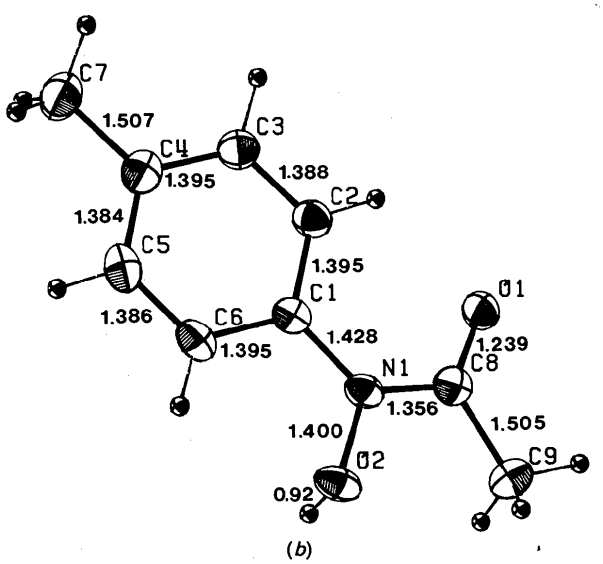
Discussion. The final atomic parameters for the two structural isomers are listed in Table 1. *ORTEP* plots (Johnson, 1976) of a single molecule of MTH and MPA are shown in Fig. 1(*a*), (*b*); included are the atom-numbering schemes and bond distances. Bond angles and selected torsion angles for each molecule are presented in Table 2.* The main structural results for MTH, obtained earlier (Kalinin *et al.*, 1982) have been confirmed, while some improvement has been achieved for the geometric parameters of the molecule.

* Lists of anisotropic thermal parameters, H-atom parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52454 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In both MTH and MPA molecules, the hydroxamic acid moiety assumes the *trans* conformation, as observed in all secondary hydroxamates reported to date (selected dimensional and conformational parameters are given in Table 3*a*,*b*); however, the interchange of the hydroxamate substituents in MTH and MPA has a pronounced effect on the planarity and dimensions (and the solution chemistry) of the hydroxamate functionality. In MTH, the protonated hydroxamate is significantly non-planar, with a r.m.s. deviation of the atoms



(*a*)



(*b*)

Fig. 1. *ORTEP* plots of single molecules of (*a*) *N*-methyl-*p*-toluohydroxamic acid (MTH) and (*b*) *N*-(4-methylphenyl)-acetohydroxamic acid (MPA). Atom-numbering schemes and bond distances (e.s.d.'s in the range 0·001–0·002 Å) are included.

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

MTH		MPA	
O(2)—N(1)—C(8)	119·1 (1)	O(2)—N(1)—C(8)	116·4 (1)
O(2)—N(1)—C(9)	114·1 (1)	O(2)—N(1)—C(1)	115·1 (1)
C(8)—N(1)—C(9)	122·7 (1)	C(1)—N(1)—C(8)	128·5 (2)
N(1)—C(8)—O(1)	119·0 (1)	N(1)—C(8)—O(1)	121·0 (2)
N(1)—C(8)—C(1)	120·9 (1)	N(1)—C(8)—C(9)	116·9 (2)
O(1)—C(8)—C(1)	120·1 (1)	O(1)—C(8)—C(9)	122·1 (2)
C(8)—C(1)—C(2)	117·1 (1)	N(1)—C(1)—C(2)	122·4 (2)
C(8)—C(1)—C(6)	123·8 (1)	N(1)—C(1)—C(6)	118·8 (2)
C(2)—C(1)—C(6)	118·8 (1)	C(2)—C(1)—C(6)	118·8 (2)
C(1)—C(2)—C(3)	121·0 (1)	C(1)—C(2)—C(3)	119·8 (2)
C(2)—C(3)—C(4)	120·7 (1)	C(2)—C(3)—C(4)	122·1 (2)
C(3)—C(4)—C(5)	118·0 (1)	C(3)—C(4)—C(5)	116·8 (2)
C(3)—C(4)—C(7)	120·5 (1)	C(3)—C(4)—C(7)	121·5 (2)
C(5)—C(4)—C(7)	121·5 (1)	C(5)—C(4)—C(7)	121·6 (2)
C(4)—C(5)—C(6)	121·8 (1)	C(4)—C(5)—C(6)	122·5 (2)
C(5)—C(6)—C(1)	119·7 (1)	C(5)—C(6)—C(1)	119·9 (2)
ω_1 = C(1)—C(8)—N(1)—C(9)	−177·0 (1)	C(1)—N(1)—C(8)—C(9)	−176·7 (2)
ω_2 = O(1)—C(8)—N(1)—O(2)	161·2 (1)	O(1)—C(8)—N(1)—O(2)	−179·2 (2)
ω_3 = O(1)—C(8)—N(1)—C(9)	5·1 (2)	O(1)—C(8)—N(1)—C(1)	0·7 (4)
ω_4 = C(1)—C(8)—N(1)—O(2)	−20·9 (1)	C(9)—C(8)—N(1)—O(2)	3·4 (3)
N(1)—C(8)—C(1)—C(6)	−38·2 (2)	C(8)—N(1)—C(1)—C(2)	−10·8 (3)
O(1)—C(8)—C(1)—C(2)	−34·0 (1)	O(2)—N(1)—C(1)—C(6)	−10·4 (3)

Table 3. *Selected geometrical parameters and conformational parameters of secondary hydroxamic acids*

(*a*) Selected geometrical parameters of secondary hydroxamic acids, R_1—C(O)—N(OH)—R_2

Compound	Conformation	C—N (Å)	N—O (Å)	C=O (Å)	*D** (°)	R.m.s. deviation† (Å)
(1)	*trans*	1·339 (2)	1·405 (2)	1·244 (1)	80	0·094
(2)	*trans*	1·356 (3)	1·400 (3)	1·239 (3)	89	0·004
(3)	*trans*	1·361 (3)	1·402 (2)	1·236 (2)	71	0·036
(4)	*trans*	1·352 (5)	1·405 (4)	1·240 (5)	76	0·026
(5)	*trans*	1·365 (4)	1·393 (5)	1·228 (5)	76	0·031
(6)	*trans*	1·328 (2)	1·396 (2)	1·241 (2)	88	0·014

(*b*) Conformational parameters of secondary *trans* hydroxamic acids

$\omega_1 = R_1$—C—N—R_2; $\chi_c = \pi + \omega_1 - \omega_3$; ω_2 = O(1)—C—H—O(2); $\chi_N = \pi + \omega_2 - \omega_3$; ω_3 = O(1)—C—N—R_2; $\tau' = \omega_1 + \omega_2$ (mod 2π).

Compound	χ_c	χ_N	τ'	P‡
(1)	−2·1	−23·9	−15·8	43·8
(2)	2·6	0·1	−4·0	10·3
(3)	1·8	8·0	−7·6	5·5
(4)	0·8	4·9	−5·0	5·0
(5)	0·3	−1·6	10·4	14·0

(1) MTH (present work). (2) MPA (present work). (3) *N*-(4-Acetylphenyl)-acetohydroxamic acid (Powell & van der Helm, 1987). (4) *N*-(3-Cyanophenyl)acetohydroxamic acid (Mocharla, Powell & van der Helm, 1984). (5) *N*-(4-Cyanophenyl)acetohydrozamic acid (Mocherla, Powell, Barnes & van der Helm, 1983). (6) *N*,*N*′-Dihydroxy-*N*,*N*′-diisopropyl-hexanediamide (Smith & Raymond, 1980).

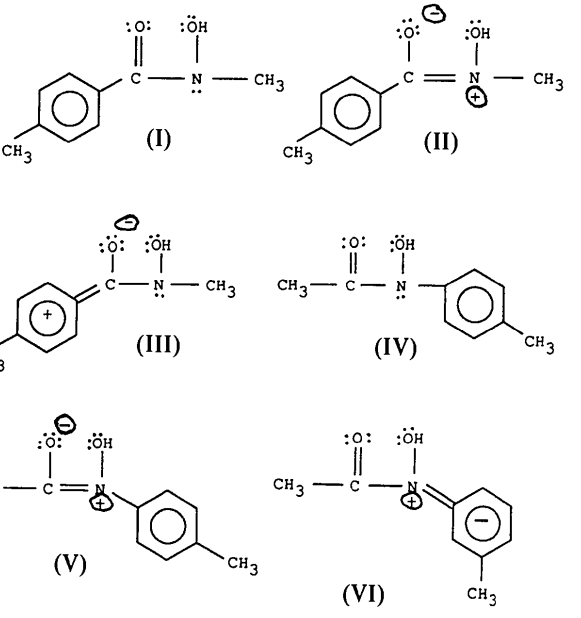
* Dihedral angle between N—O—H group and hydroxamate plane.
† From the plane through C(O)—N—O plane.
‡ P = dihedral angle between phenyl ring and hydroxamic plane.

from the plane made by O(1)—C(8)—N(1)—O(2) of 0·094 Å; in MPA, this deviation is 0·004 Å which compares favorably with the planarity observed in other secondary hydroxamic acids (range 0·004–0·036 Å, Table 3*a*).

The MTH molecule possesses a large pyramidization at N(1) (χ_N is equal to −23·9°) and a significant twist about the C(8)—N(1) bond (τ' of 15·8°,

Table 3*b*) compared to other secondary hydroxamic acids (excluding MTH) where generally smaller values of χ_N and τ' have been observed (average values of 3·6 and 6·8°, respectively). The unusual degree of N-atom pyramidization observed in MTH appears not to arise from the strong intermolecular packing forces in MTH, but rather from electronic effects brought on by the electron enrichment of one lobe of the π orbital of the hydroxamate N(1) atom by the strong inductive effect of the adjacent methyl group. This inductive influence manifests itself in two ways. Firstly, it would force the N(1)—O(2) bond below the least-squares plane made by the atoms C(1), C(8), O(1), N(1), C(9) leaving the oxime oxygen, O(2), −0·388 Å out of the plane, and secondly, it would lead to an electronic interaction with the O(2)—H(10) dipole moment which lies nearly perpendicular to the plane [H(10) lies +0·435 Å above the plane], as schematically illustrated in Fig. 2. A similar hypothesis was advanced for N-atom pyramidization in 3-hydroxyxanthine and hydroxyurea by Thiessen, Levy & Flaig (1978). Pyramidization of the hydroxamate N atom (introduction of sp^3 character) does not, however, appear to be a prevalent feature in other secondary hydroxamic acids (Table 3*b*). Furthermore, the assertion made by Thiessen and co-workers that pyramidization arises from the fact that the O—H bond of the N—OH group lies perpendicular to the hydroxamate plane seems untenable since this dihedral angle is only 80° in MMP and is closer to 90° (89° in MPA) in other secondary hydroxamic acids which exhibit no N-atom pyramidization.

A second difference between MTH and MPA arising from the interchange of R_1 and R_2 concerns the dimensions of the hydroxamate group. The largest difference is observed for the C—N distance in the two compounds. This distance is 1·339 (2) Å in MTH and 8σ shorter than in MPA [1·356 (2) Å]. A smaller but correlated difference is observed for the C=O distance which is slightly longer in MTH [1·244 (1) Å] than in MPA [1·239 (3) Å]. These observations indicate together that delocalization of the nitrogen lone pair of electrons into the C—N bond (and towards the carbonyl O atom) is more extensive in MTH than in MPA due to the large inductive effect of the CH_3 group (R_2) as shown in (II) below.



The negative formal charge on the carbonyl oxygen, O(1), can also be stabilized by electron-releasing effects from resonance of the 4-methylphenyl group (R_1) on C(8), as suggested by the general resonance form (III). Brink & Crumbliss (1984) suggest that the 4-methylphenyl group does not act as a resonance donor in MTH [therefore diminishing the contribution of resonance form (III)] due to inhibition by the strong inductive effect of the CH_3 substituent; clearly, while resonance stabilization may contribute only to a small extent, the electron donation by the 4-methylphenyl group is limited by the lack of coplanarity of the phenyl and hydroxamate planes. In MTH, the dihedral angle between the two planes is 43·8° (in MPA, it is 10·3°). Thus, while both substituents in MTH act additively in releasing electron density to the hydroxamate group, the inductive effect of the methyl group (R_2) on the delocalization of the nitrogen lone pair into the C(8)—N(1) bond seems to be the dominant effect.

In MPA, the 4-methylphenyl substituent can influence the delocalization of the nitrogen lone pair both inductively (V) and *via* resonance (VI); however, it appears to exert a smaller inductive effect than the methyl group in MTH. Further, the contribution of (VI) and the fact that the phenyl ring is nearly coplanar with the hydroxamate plane (dihedral angle of about 10°) would certainly contri-

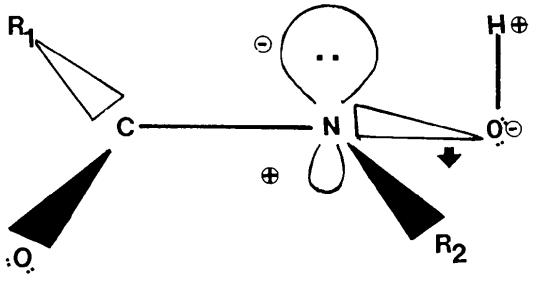


Fig. 2. Schematic diagram of a secondary hydroxamic acid group, viewed perpendicular to the C—N bond, indicating the electronic interactions arising from N-atom pyramidization.

bute to the longer C—N and shorter C=O in MPA, as compared to MTH.

These structural differences are reflected in the solution chemistry of MTH and MPA. Brink & Crumbliss (1982) and Brink, Fish & Crumbliss (1985) found that the oxime proton (NO—H) of MTH was more acidic ($pK_a = 8{\cdot}50$) than that of MPA ($pK_a = 8{\cdot}81$); these differences were rationalized in terms of the stabilization of the conjugate base by charge delocalization and entropy effects. More importantly, the interchange of substituents results in significant differences in the affinity of these ligands for the ferric ion. MTH exhibits a formation constant for the (monohydroxamato)iron(III) complex of 1441, as opposed to 294 for MPA (Brink & Crumbliss, 1984). This difference is attributed to the greater stabilization of the negative formal charge on the carbonyl oxygen atom, O(1), induced by the greater inductive effect of the MTH methyl substituent.

Finally, it should be noted that while the difference may not be statistically significant, a plot (Fig. 3) of the C—N *versus* C=O bond distances, found in Table 3(*a*) for a series of *N*-phenyl-substituted acetohydroxamic acids, follows an inverse linear relationship with decreasing electron-withdrawing ability of R_2, and, at the same time, an apparent relationship exists between the formation constant (K_f) for the (monohydroxamato)iron(III) complex (from Brink & Crumbliss, 1984, given in parentheses in Fig. 3) and the C=O bond distance. A similar observation about the C—N and C=O distances in hydroxamate acids was recently made by Kjøller Larsen (1988). These trends are anticipated and are easily rationalized in terms of the extent of delocalization of the lone pair of electrons on the hydroxamate nitrogen.

In both structures, a strong O(2)—H···O(1) hydrogen bond links the molecules in infinite chains. The molecular arrangement within a single chain in both structures is strikingly similar, although the manner in which the individual chains pack in the crystal is quite different (Fig. 4*a*,*b*). In the MTH structure, the long axes of all the molecules in the entire crystal lie approximately parallel to each other, whereas, in MPA, the molecules are arranged in a helical pattern along the *c* axis. The hydrogen-bond parameters in the two structures are very similar: O(2)···O(1) = 2·642 (2) and 2·642 (3) Å, O(2)—H = 0·92 (2) and 0·92 (2) Å, H···O(1) = 1·74 (2) and 1·72 (2) Å, and angle O(2)—H···O(1) = 167 (1) and 172 (2)° for MTH and MPA respectively.

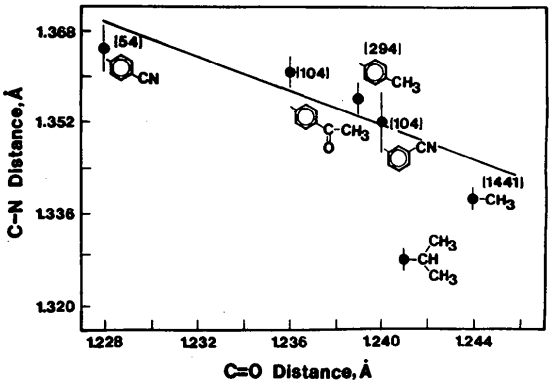


Fig. 3. Plot of C—N *versus* C=O bond distances for the hydroxamic acid groups of some secondary hydroxamic acids (see Table 3*a*) as a function of decreasing electron-withdrawing ability of the N-atom substituent (R_2). Error bars indicate the e.s.d.'s of the C—N bonds. Values of the formation constant for formation of the (monohydroxamato)iron(III) complex are given in parentheses (Brink & Crumbliss, 1984).

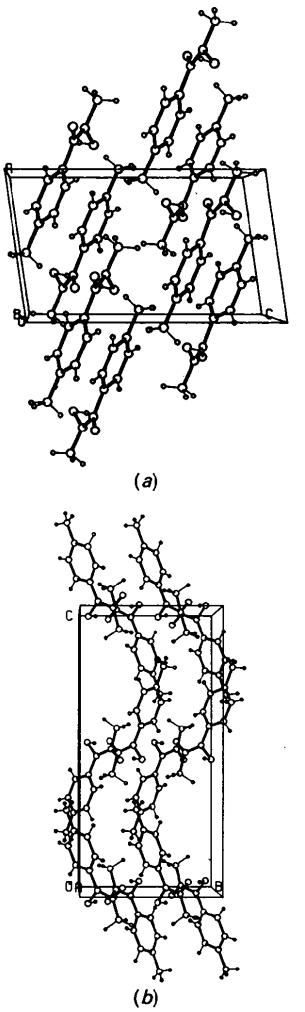


Fig. 4. Crystal packing diagrams for (*a*) *N*-methyl-*p*-toluohydroxamic acid (MTH) and (*b*) *N*-(4-methylphenyl)acetohydroxamic acid (MPA).

This work was supported by a grant from the National Institute for General Medical Sciences (GM-21822). We wish to thank Dr A. L. Crumbliss, Department of Chemistry, Duke University, for the gift of a sample of MPA.

References

AGARWAL, Y. K. (1980). *Rev. Anal. Chem.* **5**, 3–13.

BRINK, C. P. & CRUMBLISS, A. L. (1982). *J. Org. Chem.* **7**, 1171–1176.

BRINK, C. P. & CRUMBLISS, A. L. (1984). *Inorg. Chem.* **23**, 4708–4718.

BRINK, C. P., FISH, L. L. & CRUMBLISS, A. L. (1985). *J. Org. Chem.* **50**, 2277–2281.

CHATTERJEE, B. (1978). *Coord. Chem. Rev.* **26**, 281–303.

GUPTA, V. K. & TANDON, S. G. (1969). *J. Indian Chem. Soc.* **46**, 831–834.

HIDER, R. C. (1984). *Siderophores from Microorganisms and Plants*. In *Structure and Bonding*, Vol. 58, pp. 25–88. Berlin: Springer-Verlag.

JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KALININ, V. N., ANTIPIN, M. YU., YURCHENKO, V. M. & STRUCHKOW, YU. T. (1982). *Zh. Strukt. Khim.* **23**, 83–87.

KEHL, H. (1982). Editor. *Chemistry and Biology of Hydroxamic Acids*. New York: Karger.

KJØLLER LARSEN, I. (1988). *Acta Cryst.* B**44**, 527–533.

MAIN, P., FISKE, S. J., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCQ, J.-P. & WOOLFSON, M. M. (1980). *MULTAN80. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.

MOCHARLA, R., POWELL, D. R. & VAN DER HELM, D. (1984). *Acta Cryst.* C**40**, 1369–1371.

MOCHERLA, R. R., POWELL, D. R., BARNES, C. L. & VAN DER HELM, D. (1983). *Acta Cryst.* C**39**, 868–871.

MONZYK, B. & CRUMBLISS, A. L. (1979). *J. Am. Chem. Soc.* **101**, 6203–6213.

MONZYK, B. & CRUMBLISS, A. L. (1980). *J Org. Chem.* **45**, 4670–4675.

POWELL, D. R. & VAN DER HELM, D. (1987). *Acta Cryst.* C**43**, 493–495.

SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

SMITH, W. L. & RAYMOND, K. N. (1980). *J. Am. Chem. Soc.* **102**, 1252–1255.

THIESSEN, W. E., LEVY, H. A. & FLAIG, B. D. (1978). *Acta Cryst.* B**34**, 2495–2502.

Acta Cryst. (1990). C**46**, 821–823

Structure of a 1,3-Dicyanoazimine

BY KENTARO YAMAGUCHI, AKIO OHSAWA,* TERUMITSU KAIHOH, TAKASHI ITOH AND CHIKAKO KAWABATA

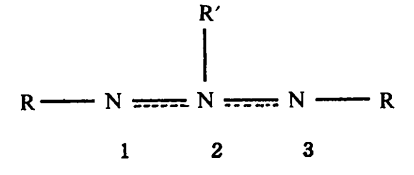
School of Pharmaceutical Sciences, Showa University 1-5-8, *Hatanodai, Shinagawa-ku, Tokyo* 142, *Japan*

(*Received* 16 *June* 1989; *accepted* 14 *August* 1989)

Abstract. (*E,Z*)-1,3-Dicyano-2-phenylazimine, $C_8H_5N_5$, $M_r = 171{\cdot}1$, monoclinic, $P2_1/a$, $a = 17{\cdot}450\ (3)$, $b = 6{\cdot}151\ (2)$, $c = 7{\cdot}871\ (1)$ Å, $\beta = 91{\cdot}61\ (1)°$, $V = 844{\cdot}5\ (4)$ Å^3, $Z = 4$, $D_x = 1{\cdot}346$ Mg m^{-3}, $\lambda(\text{Cu } K\alpha_1) = 1{\cdot}54050$ Å, $\mu = 0{\cdot}764$ mm^{-1}, $F(000) = 352$, $T = 293$ K, final $R = 0{\cdot}048$ for 1170 reflexions. The (*E,Z*)-conformation and a true dipolar system were observed. In the crystal structure, the molecules within a column are held together by the perpendicular stacking and no intermolecular hydrogen bonds or short non-bonded contacts are observed.

Introduction. The 1,3-dipolar azimines, acyclic isomers of triaziridines, have attracted considerable interest in the theoretical characterization of polyaza compounds (Nguyen, Kaneti, Hoesch & Dreiding, 1984).

1,3-Dicyano-2-phenylazimine (I) is the first example which contains an identical substituent (—C≡N) in the 1 and 3 positions. The present paper describes details of the structure analysis of (I) which makes a contribution to the theoretical studies of *E–Z* isomerization in this class of compound.



(I) R′ = Ph, R = CN

Experimental. Compound (I) was prepared by oxidation of 4,5-diamino-2-phenyl-1,2,3-triazole (Thiele & Schleussner, 1897) using $Pb(OAc)_4$ in CH_2Cl_2. Recrystallization from $C_2H_5OC_2H_5/C_6H_{14}$ gave colorless prisms having m.p. 364–364·5 K. The combustion analysis of this compound was consistent with the structure. Intensity data collected from a crystal of dimensions 0·35 × 0·08 × 0·55 mm.

* To whom correspondence should be addressed.

0108-2701/90/050821-03$03.00