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Structure of 1,6-Dioxa-6a-thiapentalene, $C_5H_4O_2S$, and Comparison with a New Structure Refinement of 2,5-Diaza-1,6-dioxa-6a-thiapentalene, $C_3H_2N_2O_2S$, from X-ray and Neutron Data at 122 K. Preliminary Charge-Density Study

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Abstract

1,6-Dioxa-6a-thiapentalene (I), $M_r = 128\cdot1$, monoclinic, Pc, $a = 6\cdot774\,(5)$, $b = 3\cdot875\,(3)$, $c = 11\cdot033\,(7)$ Å, $\beta = 108\cdot90\,(5)^\circ$, $V = 274\,(1)$ Å^3, $Z = 2$, $D_x = 1\cdot55$ Mg m^{-3}, Zr-filtered Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot048$ mm^{-1}, $F(000) = 132$, $T = 293$ K, $wR = 0\cdot036$ for 731 observed reflections. 2,5-Diaza-1,6-dioxa-6a-thiapentalene (II) (new refinement at 122 K), $M_r = 130\cdot1$, monoclinic, $P2_1/c$, $a = 6\cdot836\,(3)$, $b = 6\cdot955\,(3)$, $c = 10\cdot953\,(5)$ Å, $\beta = 111\cdot90\,(5)^\circ$, $V = 483\,(1)$ Å^3, $Z = 4$, $D_x = 1\cdot79$ Mg m^{-3}, Zr-filtered Mo $K\alpha$ radiation, $\lambda = 0\cdot71069$ Å, $\mu = 0\cdot054$ mm^{-1}, $F(000) = 264$, $T = 122$ K, $wR = 0\cdot044$ for 3062 reflections; neutron radiation, $\lambda = 0\cdot844$ Å, $\mu = 0\cdot07$ mm^{-1}, $wR = 0\cdot074$ for 1677 reflections. In both structures, as was previously observed in (II) at 293 K, the molecules are planar and have no crystallographic symmetry elements. An unusually short H$\cdots$N contact of 2·30 Å is observed in (II): a corresponding C—H$\cdots$N angle close to 180° suggests a weak hydrogen-bond type of interaction. Short S$\cdots$O contacts of 1·83–1·88 Å, longer than the normal covalent S—O bond but much shorter than the sum of the van der Waals radii, are observed in both compounds. A preliminary experimental deformation electron density map is obtained for compound (II) from a combined X-ray and neutron

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data ($X + N$) refinement with a radial deformation density model. It shows well known features of C—C and C—N bonds, while the O···S···O region is diffuse and very little positive density corresponding to lone pairs is observed around O atoms. This would indicate that O is nearly in a spherical state with little hybridization, contrary to theoretical results obtained by local-density-function calculations.

1. Introduction

This work is part of a series of structural and charge-density studies on compounds involving short unusual S···O bonds (Cohen-Addad, Savariault & Lehmann, 1981; Cohen-Addad, Lehmann, Becker, Párkányi & Kálmán, 1984; Becker, Cohen-Addad, Delley, Hirshfeld & Lehmann, 1986). Short contacts of the type X—S···O (X = C, O, S) have been observed in many compounds (Kálmán & Párkányi, 1980; Pedersen, 1980; Bernardi, Csizmadia & Mangini, 1985). The S···O distances range from 1·85 to 2·96 Å, which is larger than the covalent S—O bond length of 1·56–1·65 Å (Bernardi *et al.*, 1985), yet much smaller than the sum of the van der Waals radii, which is 3·3 Å (Pauling, 1960). In previous studies on compounds with S···O contacts of 2·24 and 2·68 Å (Cohen-Addad *et al.*, 1981, 1984), the X–N deformation electron density maps showed only weak features around oxygen, notably for the lone-pair regions; theoretical analysis showed that in these compounds the X—S···O attraction is mainly due to interactions between p orbitals of the O atom and p and d orbitals of the S atom. Moreover, the different S···O distances could be related to the electronegativity of the X atoms with the shortening being greatest for X = O.

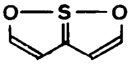
Following this, it seemed useful to undertake a study of the limiting case of very short S···O contacts as found in derivatives of thiapentalene. In these compounds, for which several crystal structures are known (Dalseng, Hansen & Hordvik, 1981; Amundsen, Hansen & Hordvik, 1982), the X—S···O system is O···S···O and the two S···O lengths are similar with a value of about 1·87 Å. Furthermore, these molecules are planar and show a symmetrical conjugated structure.

Two compounds are investigated in the present paper:

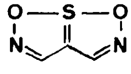
(*a*) 1,6-Dioxa-6a-thiapentalene (I) has been extensively studied by spectroscopic methods (^{1}H NMR and microwave spectra) which indicate a C_{2v} symmetry in the gas phase and in solution (Pedersen, 1980, and references cited therein). Its crystal structure, which remained unknown, is determined and described in the present work.

(*b*) The crystal structure of 2,5-diaza-1,6-dioxa-6a-thiapentalene (II) was previously determined at room temperature (Amundsen *et al.*, 1982). In the thiapentalene series, (II) represents a good choice for charge-density studies (centrosymmetric structure, no disorder, no phase transition at low temperature, large-size crystals of good quality suitable for a neutron diffraction study). We undertook X-ray and neutron diffraction studies of this compound at 122 K. A theoretical study using the local-density-function method and extended-Hückel calculations is described elsewhere (Becker *et al.*, 1986). In the present paper, the experimental results and accurate structural characteristics are given and compared with those of the closely related compounds (I) and 2,5-dimethyl-1,6-dioxa-6a-thiapentalene (III) (Dalseng *et al.*, 1981).

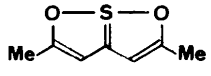
Preliminary results on the deformation electron density are also given.



(I)



(II)



(III)

2. Experimental

2.1. *Compound* (I)

The compound was kindly supplied by Dr C. Th. Pedersen. One colourless crystal, 0·4 × 0·45 × 0·65 mm, obtained with great difficulty by sublimation in a vacuum-sealed glass tube and kept in a capillary to prevent sublimation (the crystal was not stable, however, over a very long period). Measurements with a Siemens diffractometer. Zr-filtered Mo $K\alpha$ radiation, five-point method (Hoppe, 1965), $\theta/2\theta$ scan, no absorption correction. Lattice parameters refined with 13 reflections, $11 < \theta < 19°$. 731 independent reflections with $I > 3\sigma(I)$ (954 measured), $\sin\theta/\lambda \leq 0{\cdot}7$ Å^{-1}; hkl, $\bar{h}kl$, h −9 to 9, k 0 to 5, l 0 to 15. Standard reflections $\bar{4}25$, $\bar{3}16$, $\bar{2}$,0,10 (3% variation). Structure solved by multisolution direct methods (Germain, Main & Woolfson, 1971). Least-squares refinement minimizing $\sum w(F_o - F_c)^2$ (program *XFLS*; Busing & Levy, 1962). No extinction correction (negligible). Positional and anisotropic parameters refined for heavy atoms; H-atom positional parameters calculated (not refined); isotropic temperature factors for H estimated (not refined). Weighting scheme obtained empirically by plotting $(F_o - F_c)^2$ as a function of F_o (Rollett, 1965). Final $R = 0{\cdot}030$, $wR = 0{\cdot}036$ for 731 reflections. $(\Delta/\sigma)_{\max} = 0{\cdot}8$, final $\Delta\rho < 0{\cdot}25$ e Å^{-3}. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Final parameters given in Table 1.*

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* Lists of structure factors, mean-planes data, H-atom parameters and anisotropic thermal parameters for compounds (I) and (II) have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44873 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. 1,6-*Dioxa-6a-thiapentalene* (I): *atomic coordinates* (× 10^4)

$B_{eq} = 8\pi^2(U_1U_2U_3)^{2/3}$.

	x	y	z	B_{eq} (Å^2)
S	5000 (0)	3446 (2)	2500 (0)	3·6
O(1)	2265 (3)	4984 (7)	1750 (2)	5·0
O(6)	7763 (3)	1790 (7)	3096 (2)	4·5
C(2)	1710 (5)	4507 (10)	524 (4)	4·8
C(3)	3106 (5)	3034 (9)	42 (3)	4·2
C(3a)	4985 (4)	2326 (6)	1001 (2)	3·0
C(4)	6854 (5)	879 (8)	961 (3)	4·0
C(5)	8291 (4)	673 (9)	2128 (3)	4·6

Table 2. 2,5-*Diaza*-1,6-*dioxa-6a-thiapentalene* (II): *atomic coordinates* (×10^5) *from* ($X + N$) *radial refinement at* 122 K

$B_{eq} = 8\pi^2(U_1U_2U_3)^{2/3}$.

	x	y	z	B_{eq} (Å^2)	Charge (e)	κ
S	76616 (4)	9586 (3)	7386 (2)	1·11 (2)	0·35 (8)	1·004 (9)
O(1)	77549 (9)	−12993 (8)	−1036 (5)	1·57 (3)	0·36 (3)	1·034 (8)
O(6)	74267 (10)	30026 (8)	17364 (5)	1·51 (3)	0·26 (4)	1·034 (4)
N(2)	76240 (8)	−28724 (6)	5657 (4)	1·53 (3)	−0·28 (5)	0·974 (5)
N(5)	71987 (8)	24915 (6)	28519 (4)	1·50 (3)	−0·47 (5)	0·974 (5)
C(3)	74763 (9)	−24187 (7)	16942 (5)	1·26 (3)	−0·19 (6)	1·034 (7)
C(3a)	74603 (8)	−4320 (7)	19415 (4)	0·98 (3)	0·37 (7)	1·080 (11)
C(4)	72367 (9)	6121 (7)	29849 (5)	1·27 (3)	−0·36 (7)	1·034 (7)
H(3)	73620 (30)	−35550 (20)	23390 (20)	2·60 (10)	0·04 (3)	1·000
H(4)	70970 (30)	−100 (30)	38590 (20)	2·60 (10)	−0·08 (3)	1·000

Additional overall isotropic thermal parameter for X-ray data: $B =$ 0·166 (8) Å^2.

2.2. *Compound* (II)

The compound was synthesized in a hydrochloric acid solution from 1,3-propanedial dioxime in the presence of thionyl chloride (Larsen, Nygaard, Pedersen, Pedersen & Davy, 1984). Crystals were grown by evaporation from cyclohexane solution in a refrigerator.

X-ray data collection. Yellow crystal, 0·3 × 0·35 × 0·4 mm, enclosed in capillary to avoid sublimation. 7787 reflections measured with a Siemens four-circle diffractometer at 122 K, using a gas-flow cooling system. Temperature calibration used the phase transition of KH_2PO_4 at 122·4 K. Zr-filtered Mo $K\alpha$ radiation, five-point method (Hoppe, 1965), $\theta/2\theta$ scan mode, absorption correction by Gaussian integration (Coppens, Leiserowitz & Rabinovich, 1965), transmission factors 0·87–0·91. Lattice parameters refined with 21 reflections, $12 < \theta < 24°$, $\sin\theta/\lambda \leq 0·92$ Å^{-1}; hkl, $h\bar{k}\bar{l}$, $hk\bar{l}$, $h\bar{k}l$, h 0 to 12, k −12 to 12, l −19 to 19. Standard reflections 319, 034, 242 (2·5% variation corrected). 3062 independent reflections after averaging. $R_{int} = 0·015$ for $\sin\theta/\lambda \leq 0·57$ Å^{-1} and 0·048 for the rest of the data.

Neutron data collection. Crystal, 4 × 1·5 × 0·7 mm. 2744 reflections measured on the four-circle diffractometer D9 of the Institut Laue–Langevin using a displex refrigerator (Allibon, Filhol, Lehmann, Mason & Simms, 1981) for cooling to 122 K. Wavelength 0·844 Å, θ–2θ step scanning used with 40 steps and data reduction by minimal $\sigma(I)/I$ (Lehmann & Larsen, 1974). Absorption correction (Coppens *et al.*, 1965), transmission factors 0·88–0·95. $\mathrm{Sin}\theta/\lambda \leq 0·76$ Å^{-1}; $\bar{h}kl$, $\bar{h}k\bar{l}$, h −10 to 0, k −10 to 0, l −16 to 16. Standard reflection $\bar{2}00$ (no variation). 1677 independent reflections after averaging, $R_{int} = 0·022$.

Separate X-ray (X) *and neutron* (N) *data refinements.* Refinements using squared structure amplitudes were carried out separately on the X-ray and the neutron data. *XFLS* (Busing & Levy, 1962) was used. Form factors, including the anomalous X-ray scattering of O and S were taken from *International Tables for X-ray Crystallography* (1974), while the neutron-scattering lengths were taken from the compilation by Koester & Rauch (1981). An isotropic extinction correction was included. Final discrepancy indices, $R = \sum F_o - F_c/\sum F_o$ and $wR = [\sum w(F_o{}^2 - F_c{}^2)^2/\sum wF_o{}^4]^{1/2}$, were for the X-ray refinement $R = 0·063$, $wR = 0·074$ for 3062 reflections, $(\Delta/\sigma)_{max} = 0·3$ for heavy atoms and 0·8 for H atoms, $w = [\sigma^2(F^2)]^{-1} = [\sigma^2_{obs}(F^2) + 10^{-4}F^4 + 1·3 \times 10^{-6}F^6]^{-1}$;* and for the neutron refinement $R = 0·039$, $wR = 0·064$ for 1677 reflections, $(\Delta/\sigma)_{max} = 0·2$, $w = [\sigma^2_{obs}(F^2) + 9 \times 10^{-4}F^4]^{-1}$. The extinction effects were negligible for the X-ray data, and very small for the neutron data (correction greater than 2% for only 20 reflections).

X–N difference electron density maps were calculated using the neutron results for both atomic poitions and thermal parameters. They showed the expected positive bond regions, but a large peak was found near the S atom. The site and shape of this peak were very sensitive to the neutron thermal parameters. As the neutron-scattering length of S is relatively small, the atomic parameters determined by neutrons are much less precise than those from the X-ray data. It was therefore decided to obtain the structural parameters from a joint ($X + N$) refinement of both data sets (Coppens, Boehme, Price & Stevens, 1981).

Joint ($X + N$) *refinement with radial deformation.* A comparison between the X-ray and neutron thermal parameters showed the latter to be smaller by an average of about $B = 0·15$ Å^2. To take this into account, an overall isotropic difference thermal parameter was included in the joint refinement of X-ray and neutron data. If all X-ray reflections are included in a joint refinement, the resulting parameters will be biased by the deviation of the electron density from the distribution in non-bonded atoms. To compensate partially for this, we carried out a refinement using a radial deformation model (computer program *RADIEL*; Coppens, Guru Row, Leung, Stevens, Becker & Yang, 1979). In this model the population of the valence electrons, p, for each atom is varied together with a contraction–expansion parameter κ, and the valence-electron distribution has the form:

$$\rho'(r) = p\kappa^3\rho(\kappa r)$$

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* From F. Hirshfeld (private communication).

Table 3. *Interatomic distances* (Å) *and bond angles* (°) *for compounds* (I) *and* (II) *with e.s.d.'s in parentheses*

Compound (I)			
S–O(1)	1·866 (2)	O(6)–S–O(1)	174·4 (1)
S–O(6)	1·885 (2)	O(6)–S–C(3a)	86·9 (1)
S–C(3a)	1·706 (2)	O(1)–S–C(3a)	87·5 (1)
O(1)–C(2)	1·295 (2)	S–O(1)–C(2)	109·2 (2)
O(6)–C(5)	1·304 (5)	S–O(6)–C(5)	109·4 (2)
C(2)–C(3)	1·352 (5)	O(1)–C(2)–C(3)	117·8 (2)
C(5)–C(4)	1·342 (4)	O(6)–C(5)–C(4)	117·4 (2)
C(3a)–C(3)	1·395 (4)	C(2)–C(3)–C(3a)	115·5 (3)
C(3a)–C(4)	1·398 (4)	C(5)–C(4)–C(3a)	112·1 (2)
		S–C(3a)–C(3)	113·8 (2)
		S–C(3a)–C(4)	114·2 (2)
		C(3)–C(3a)–C(4)	131·9 (2)
Compound (II)			
S–O(1)	1·8344 (9)	O(6)–S–O(1)	171·56 (3)
S–O(6)	1·8364 (9)	O(6)–S–C(3a)	85·87 (3)
S–C(3a)	1·6809 (8)	O(1)–S–C(3a)	85·98 (4)
O(1)–N(2)	1·3384 (10)	S–O(1)- N(2)	113·73 (4)
O(6)–N(5)	1·3360 (10)	S–O(6)–N(5)	113·84 (5)
N(2)–C(3)	1·3160 (9)	O(1)–N(2)–C(3)	111·27 (5)
N(5)–C(4)	1·3144 (9)	O(6)–N(5)–C(4)	111·20 (5)
C(3a)–C(3)	1·4089 (9)	N(2)–C(3)–C(3a)	115·13 (5)
C(3a)–C(4)	1·4097 (9)	N(5)–C(4)–C(3a)	115·22 (5)
C(3)–H(3)	1·0820 (20)	S–C(3a)–C(3)	113·88 (5)
C(4)–H(4)	1·0870 (20)	S–C(3a)–C(4)	113·85 (5)
C(3a)–C(3)–H(3)	125·70 (10)	C(3)–C(3a)–C(4)	132·22 (5)
C(3a)–C(4)–H(4)	125·50 (10)	N(2)–C(3)–H(3)	119·20 (10)
		N(5)–C(4)–H(4)	119·20 (10)
H(3)···O(1^{i})	2·714 (2)	C(3)–H(3)···O(1^{i})	134·2 (1)
H(3)···O(6^{ii})	2·488 (2)	C(3)–H(3)···O(6^{ii})	121·1 (1)
H(4)···N(2^{i})	2·300 (2)	C(4)–H(4)···N(2^{i})	158·5 (1)
H(4)···O(1^{i})	2·775 (2)	C(4)–H(4)···O(1^{i})	132·1 (1)

Symmetry codes: (i) $x, -y-\frac{1}{2}, z$; (ii) $x, y-1, z$.

where ρ' is the modified density, and r is the distance from the atom centre. The weighting schemes were the same as in the separate refinement. Final discrepancy indices were: X-rays: $R = 0{\cdot}063$, $wR = 0{\cdot}070$, $S = 1{\cdot}3$, for all 3062 reflections; neutrons: $R = 0{\cdot}041$, $wR = 0{\cdot}059$, $S = 1{\cdot}1$, for all 1677 reflections, $(\Delta/\sigma)_{\max} = 0{\cdot}1$. Final atomic and thermal displacement parameters are given in Table 2.*

3. Discussion

3.1. *Molecular geometries and intermolecular contacts*

For both compounds, interatomic distances and angles are listed in Table 3. Conformations of the molecules are shown in Fig. 1. As expected, the standard deviations for compound (I) are larger than for compound (II), but still sufficiently small to allow meaningful chemical comparisons.

Both molecules are almost planar with a slight bending (2°) between the two rings.

In compound (I), the S–O(1) distance is significantly shorter than S–O(6), but apart from that, the geometries of the two halves, although non-crystallographically equivalent, are very similar. As in (II), (III) and trithiapentalene structures (Dalseng *et al.*, 1981), the C–O length has double-bond character and the C(2)–C(3) and C(4)–C(5) bonds are shorter than the central C(3)–C(3a) and C(4)–C(3a) bonds.

In compound (II), the geometry shows the same characteristics as in the room-temperature structure (Amundsen *et al.*, 1982), namely, two almost equal S···O distances and N–O bond lengths intermediate between the values of a single and a double bond, while C–N is near a double bond. The central S–C(3a) bond length of 1·681 Å is significantly shorter than the corresponding length observed in (I) (1·706 Å) and in (III) (1·732 Å).

In (I) normal intermolecular contacts are observed, whereas in (II) several short intermolecular contacts are found, notably one contact between H(4) and N(2) with a length of only 2·30 Å. This is unusually short for a C–H···N contact; other known interactions of the same kind have contact distances of 2·52 Å and larger (Taylor & Kennard, 1982).

The C–H···N bond angle (159°) is sufficiently large to suggest a hydrogen-bond type of interaction, and this is supported by IR observations (Mollier, 1985). In solution a narrow absorption band at 3104 cm^{-1}, characteristic of C–H stretching, is observed. In the solid state this band is weakened and a split, broadened band in the range 3104–3084 cm^{-1}, typical of hydrogen-bond formation, occurs. Other X–H···Y contacts with H···Y distances between 2·49 and 2·78 Å and X–H···Y angles far from 180° are probably best regarded as normal van der Waals interactions.

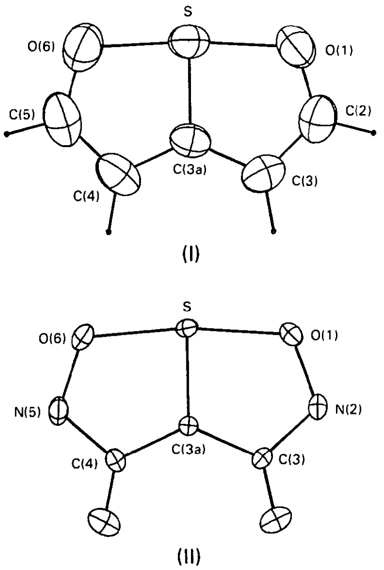

Fig. 1. Conformation of molecules (I) and (II): projection on the molecular planes. The thermal ellipsoids are drawn at 50% probability.

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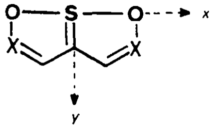
* See deposition footnote.

3.2. *Theoretical interpretation*

It was shown from extended Hückel calculations (Becker *et al.*, 1986) that there are two main contributions to the observed structures of these compounds.

(*a*) The S—O shortening is best explained by the dominance of the resonance structure (IV) which involves a hypervalent S atom, a p_y orbital being promoted to a $d_{x^2-y^2}$ state.



(IV)

(*b*) The S—C shortening mainly occurs in compound (II), where $X = \mathrm{N}$. In this respect, the π-electron structure is a compromise between the O—S and the O—X coupling. If X is more electronegative than S, as for $X = \mathrm{N}$ (II), the oxygen π pair is essentially coupled to X, and the π electron of S can participate strongly in an S=C double bond. At the same time, the accumulation of electrons around N can explain a short N···H—C intermolecular contact. If $X = \mathrm{C}$, the π-electron system is polarized towards S, and the S—C bond is longer.

3.3. *Experimental deformation electron density map of compound* (II)

The atomic and thermal displacement parameters of Table 2 were used to calculate $X - (X + N)$ deformation electron densities relative to free atoms ($\kappa = 1$). A section through the mean molecular plane is shown in Fig. 2.

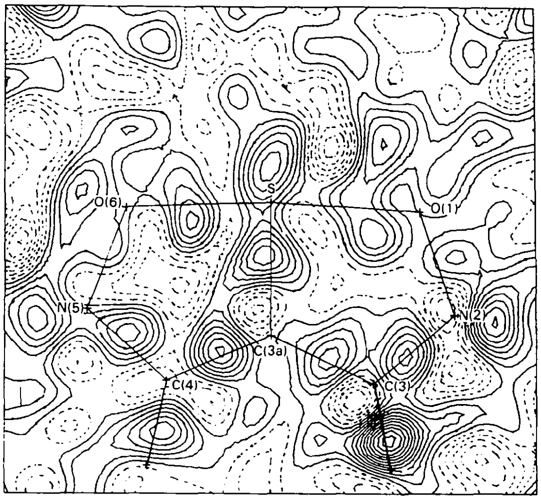


Fig. 2. Electron deformation density map for compound (II): $X - (X + N)$ map in the mean molecular plane after radial refinement, contour interval at 0·05 e Å^{-3}.

The well-known features of C—C and C—N bonds are observed, *i.e.* a peak in the centre of the bond, and a positive deformation in the region of the N lone pairs. However the O···S···O region is very diffuse and little positive density is observed in the lone-pair region for O atoms. This would indicate that O is nearly in a spherical state with little hybridization; this is in contradiction to the theoretical maps obtained by a local-density-function caculation (Becker *et al.*, 1986).

More experimental studies at very low temperature are presently in progress to clarify this point, and new results will be published soon.

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Structural Characteristics of the Hydroxamic Acid Group. Crystal Structure of Formohydroxamic Acid

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Abstract

CH_3NO_2, $M_r = 61{\cdot}04$, monoclinic, Cc, $a = 3{\cdot}636\ (3)$, $b = 9{\cdot}745\ (2)$, $c = 7{\cdot}512\ (3)$ Å, $\beta = 116{\cdot}56\ (4)°$, $V = 238{\cdot}1\ (2)$ Å^3, $Z = 4$, D_m (293 K) = 1·64, $D_x = 1{\cdot}703$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 0{\cdot}154$ mm^{-1}, $F(000) = 128$, $T = 105$ K, final $R = 0{\cdot}030$ for 995 unique observed reflections. The conformation of O=CH—NH—OH is synperiplanar (*sp*) with an O=C—N—O torsion angle of 5·4 (4)°. The crystals are stabilized by a network of intermolecular hydrogen bonds. Data for a series of hydroxamic acids, *R*CONHOH, and hydroxamate ions and ligands have been retrieved from the Cambridge Structural Database. Bond distances and bond angles as well as conformational parameters of the hydroxamic acid moiety have been analyzed. The antiperiplanar (*ap*) conformation of the O=C—NH—OH moiety is found to be almost as common in crystals as the *sp* conformation. Only one case of intramolecular OH···O bonding in *sp* conformers was found. Variations in C=O and C—N bond lengths are correlated. Charge delocalization through the entire hydroxamate moiety is observed in the ligands, but not in the ions. Opening of the O=C—N angle is most pronounced in *sp* conformers of hydroxamic acids. In hydroxamate ligands this angle is less than 120°.

Introduction

Formohydroxamic acid, HCONHOH, has been reported to show an inhibitory effect on several metal-containing enzymes, *e.g.* the iron-containing enzyme ribonucleotide reductase (Kjøller Larsen, Sjöberg & Thelander, 1982), the nickel-containing enzyme urease (Dixon, Hinds, Fihelly, Gazzola, Winzor, Blakeley & Zerner, 1980), and zinc- or manganese-containing aminopeptidases (Wilkes & Prescott, 1983; Baker, Wilkes, Bayliss & Prescott, 1983). The inhibitory effect of hydroxamic acids on ribonucleotide reductase has been shown to be due to the ability of the compounds to react with (reduce) the tyrosine free-radical group present in the subunit B2 of this enzyme (Kjøller Larsen *et al.*, 1982). Metal chelation is proposed to be important for the inhibitory effect on the other enzymes mentioned above.

An IR and ^{1}H NMR study of formohydroxamic acid and its sodium salt has been reported (Fritz & von Stetten, 1969), but no detailed experimental structural study has been made so far. On the other hand, several theoretical calculations on the geometry of formohydroxamic acid have been performed in recent years. *Ab initio* SCF MO calculations at the 3-21G level, carried out on formohydroxamic acid (Lipczyńska-Kochany & Iwamura, 1982) indicated an *sp* (synperiplanar) conformation of O=CH—NH—OH with intramolecular O—H···O bonding to be energetically most favourable. This is in agreement with the results of Bock, Trachtman & George (1981, 1982) and George, Bock & Trachtman (1983) in their extensive study of small molecules, forming intramolecular hydrogen-bonded four-, five- or six-membered ring systems, by *ab initio* MO calculations, using the 4-31G set. In addition, semiempirical INDO MO calculations (Hilal & Moustafa, 1984) led to the reverse result, as the *ap* (antiperiplanar) conformation was found to be more stable than the *sp* conformation, but the INDO method is hardly as reliable as the *ab initio* methods used by the authors mentioned above. Finally, *ab initio* calculations (STO-3G basis set) have been performed on the tautomer form (see below) of formohydroxamic acid ('hydroxyformaldoxime') by Nguyen, Sana, Leroy, Dignam & Hegarty (1980).

Hydroxamic acids exist in solutions as an equilibrium mixture of the two tautomers: *R*CONHOH (I) $\rightleftharpoons$ *R*C(OH)=NOH (II), where (I) is the hydroxyamide (or hydroxamic acid) form, and (II) the hydroxyimine (or

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