

## The Molecular Structure of Gaseous 1,3,4-Oxathiazol-2-one

BØRGE BAK,<sup>a</sup> OLE NIELSEN,<sup>a</sup> HENRIK SVANHOLT,<sup>a</sup> ARNE ALMENNINGEN,<sup>b</sup> OTTO BASTIANSEN,<sup>b</sup> LIV FERNHOLT,<sup>b</sup> GRETE GUNDERSEN,<sup>b</sup> CLAUD J. NIELSEN,<sup>b</sup> BJØRG N. CYVIN,<sup>c</sup> and SVEN J. CYVIN<sup>c</sup>

<sup>a</sup> Chemical Laboratory V, The H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen, Denmark, <sup>b</sup> Department of Chemistry, University of Oslo, Oslo 3, Norway and <sup>c</sup> Division of Physical Chemistry, University of Trondheim, N-7034 Trondheim-NTH, Norway

1,3,4-Oxathiazol-2-one has been studied by microwave, infrared and Raman spectroscopy and by electron diffraction from the vapour. The analysis of the spectroscopic data established a coplanar molecular structure. The rotational constants were  $A_0 = 5587.411(11)$ ,  $B_0 = 3645.8735(89)$  and  $C_0 = 2205.4635(89)$  MHz and the inertial defect was  $\Delta = 0.08236(57) \mu\text{Å}^2$ . The structural refinements based upon the electron-diffraction data led to three very similar sets of geometrical parameters for three different sets of fixed  $u$ -values which were derived from: I, analogy to similar molecules; II, an estimated force field; and III, from a normal coordinate analysis based upon the spectroscopic data. The electron-diffraction work also demonstrated an essentially planar molecule and produced bond distances and angles in agreement with the experimental spectroscopic rotational constants. The final refinement of a planar molecular model was carried out based upon electron-diffraction data in combination with the measured rotational constants (corrected to  $A_z$ ,  $B_z$  and  $C_z$ ). An  $r_s^0$ -model was used to account for shrinkage effects, and the  $u$ -values and the various correction terms needed were as obtained from the normal coordinate analysis. The bond distances ( $r_a$ ) and independent valence angles thus obtained are:  $r(\text{C}-\text{H}) = 1.102(19) \text{Å}$ ,  $r(\text{C}=\text{O}) = 1.192(2) \text{Å}$ ,  $r(\text{N}=\text{C}) = 1.286(2) \text{Å}$ ,  $r(\text{O}-\text{C}(\text{H})) = 1.356(3) \text{Å}$ ,  $r(\text{O}-\text{C}(=\text{O})) = 1.402(3) \text{Å}$ ,  $r(\text{S}-\text{N}) = 1.690(2) \text{Å}$ ,  $r(\text{S}-\text{C}) = 1.767(2) \text{Å}$ ,  $\angle \text{OCH} = 114.5(31)^\circ$ ,  $\angle \text{OCO} = 122.6(3)^\circ$ ,  $\angle \text{COC} = 110.8(2)^\circ$ ,  $\angle \text{CSN} = 93.8(1)^\circ$ . The parenthesized values are the estimated standard deviations including effects of correlation among the electron-diffraction data.

Knowledge of the structure of 1,3,4-oxathiazol-2-one  $\text{HC}=\text{N}-\text{S}-\text{CO}-\text{O}$ , is necessary for a future

theoretical treatment of its interesting pyrolysis.<sup>1,2</sup> Dependent upon the extent of electron delocalization the molecule is a planar or a non-planar unsubstituted 5-membered ring compound.

In this paper the results of a combined spectroscopic and electron-diffraction investigation of 1,3,4-oxathiazol-2-one will be presented. By the electron-diffraction method on gaseous molecules a three dimensional structure is determined from a one dimensional intensity curve. The Fourier inverse of the molecular intensity curve is a one dimensional radial distribution curve, the resolution of which is limited due to the widths of individual peaks. The widths of the individual peaks, depending upon the molecular vibrations, are of the order of magnitude from about 0.08 to 0.2 Å. In a molecule like 1,3,4-oxathiazol-2-one there exist altogether 21 different internuclear distances in the distance range from about 1.0 to 4.5 Å. Even if the molecule is assumed to be planar, there exist 11 independent geometrical parameters. If the vibrational parameters are included, 32 structure parameters have in the general case to be determined. Experience shows that rigid molecules of this kind give good quality electron-diffraction intensity data. The idea of the approach chosen was to try to estimate how well the electron-diffraction method could solve the geometry of a many parameter molecule with complex distance overlaps if the vibrational parameters were obtained from other approaches, and to attempt a structure refinement based upon electron-diffraction data in combination with information obtained from rotational and vibrational spectroscopy.

## EXPERIMENTAL

(a) *Sample.* 1,3,4-Oxathiazol-2-one was prepared in analogy to its methyl derivative,  $\text{CH}_3\text{-C=N-S-CO-O}$ ,<sup>3</sup> by Arne Holm, the H. C. Ørsted Institute, and purified by distillation *in vacuo* (12 Torr) at 47–48 °C. None of the recorded microwave, infrared and Raman spectra indicated the presence of impurities.

(b) *Microwave.* Microwave spectra were recorded at 50–100 mTorr and at room temperature in the 12.5–18 and 26.5–40 GHz regions using a Hewlett-Packard 8460 A MRR instrument. Stark voltages in the range 400–1600 V/cm were applied.

(c) *Infrared and Raman.* Infrared spectra were recorded of the vapour, the  $\text{CCl}_4$  solution, the pure liquid and of the unannealed and annealed solid at liquid nitrogen temperature on a Perkin-Elmer Model 225 spectrometer. Far infrared spectra of a cyclohexane solution were obtained with a fast scan Bruker Model 114C Fourier transform spectrometer over the range 400–50  $\text{cm}^{-1}$ .

Raman spectra were obtained on a modified<sup>4</sup> Cary Model 81 Raman spectrometer using the 5145 Å line from an argon ion laser for excitation. The liquid sample was studied in a sealed glass tube and polarization data were obtained.

(d) *Electron diffraction.* The electron-diffraction data were recorded in the Oslo Apparatus<sup>5</sup> for nozzle-to-plate distances of 480.32, 200.32 and 128.27 mm, using Kodak Electron Image plates and a nozzle-tip temperature of 56 °C. The electron wavelength was 0.06465 Å as calibrated against diffraction patterns of gaseous benzene using  $r_s(\text{C-C}) = 1.3975$  Å as a standard. The estimated standard deviation in the determination of the electron wavelength is 0.1 %.

The scattering patterns were transferred to intensity data in intervals of 0.25 mm while oscillating the plates on an integrating densitometer constructed by A. Almendingen and P. Molin. In order to avoid problems due to uncertainties of blackness correction for the darker regions, plates with optical densities less than 1.35 were selected for the structure analysis. The data were processed the usual way<sup>6</sup> to yield for each of the three camera distances averaged modified molecular intensity curves based upon four plates for the long and intermediate camera distances and three plates for the shorter one. The modification function used was  $s/|f'_s|/|f'_c|$ . The scattering amplitudes and phases<sup>6</sup> were calculated using the partial-wave method<sup>7</sup> based upon the analytical HF potentials for the C-, N-, O-, and S-atoms<sup>8</sup> and the best electron density of bonded hydrogen for the H-atom.<sup>9</sup> The inelastic scattering factors used were those of Tavard *et al.*<sup>10</sup>

## ANALYSIS OF MICROWAVE DATA

Approximate rotational constants,  $A'_0$ ,  $B'_0$ ,  $C'_0$ , were calculated from a preliminary unrefined structure of 1,3,4-oxathiazol-2-one provided by electron-diffraction ( $A'_0 = 5625$ ;  $B'_0 = 3628$ ;  $C'_0 = 2205$  MHz. Asymmetry parameter,  $\kappa = -0.1678$ ). Then, a number of low- $J$  transitions were identified within 5–60 MHz of their precalculated positions by their Stark patterns and their relative intensities. A revised set of rotational constants then allowed the precalculation and identification of higher- $J$  transitions. Number and types of measured transitions are summarized in Table 1 (93 transition frequencies available on request). Table 2 summarizes the final analysis in terms of ground-state rotational and distortion constants. As seen, the inertial defect  $I_c - I_b - I_a = 0.08236(57)$   $\mu\text{Å}^2$  is in accordance with inertial defects for other planar, 5-membered ring molecules.<sup>12</sup>

## VIBRATIONAL SPECTRA

The planarity of 1,3,4-oxathiazol-2-one in the vapour phase is well established from the micro-

Table 1. Number and type of observed transitions (12.5–18 and 26.5–40 GHz).  $J_{\text{max}}$  = maximum rotational quantum number. R, Q,  $\mu_a$  and  $\mu_b$  in conventional sense.

R type		Q type		ROTFIT r.m.s. <sup>a</sup>
$\mu_a$	$\mu_b$	$\mu_a$	$\mu_b$	
28	2	10	53	0.1672 MHz
8 <sup>b</sup>	7 <sup>b</sup>	27 <sup>b</sup>	30 <sup>b</sup>	

<sup>a</sup> By G. O. Sørensen, the H. C. Ørsted Institute.

<sup>b</sup>  $J_{\text{max}}$ .

Table 2. Rotational ground state constants  $A_0$ ,  $B_0$ ,  $C_0$  in MHz of 1,3,4-oxathiazol-2-one. Quartic distortion constants in kHz.<sup>a</sup> Asymmetry parameter  $\kappa$ . Inertial defect  $\Delta = I_c - I_b - I_a$  in  $\mu\text{Å}^2$ .

$$A_0 = 5587.411 \quad (11)$$

$$B_0 = 3645.8735 \quad (89)$$

$$C_0 = 2205.4635 \quad (89)$$

$$T_1 = -0.061(20); T_2 = 0.099(17); T_3 = -0.749(95)$$

$$T_4 = 1.186(22); T_5 = -0.05(10)$$

$$\kappa = -0.1481772(13); \Delta = 0.08236(57)$$

<sup>a</sup> As defined in Ref. 11.

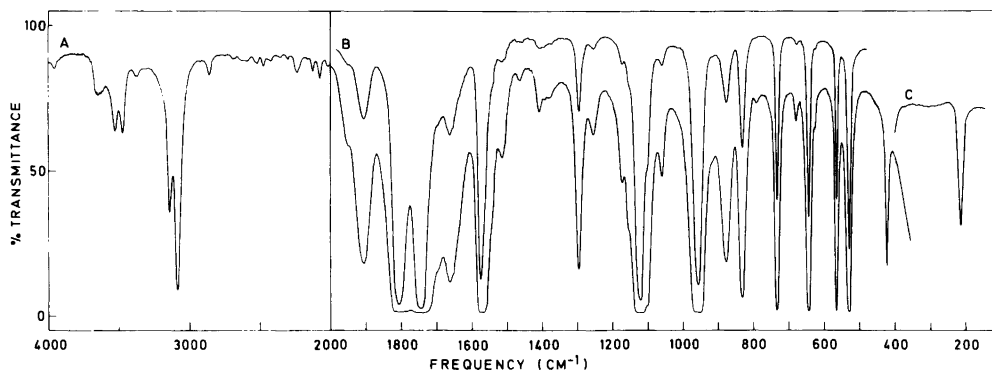


Fig. 1. Infrared spectrum of 1,3,4-oxathiazol-2-one in the liquid phase, (A) 0.025 mm cell and (B) thin film and in cyclohexane-solution (C).

wave investigation. Accordingly, the vibrational spectra can be interpreted in terms of  $C_s$  symmetry. The 15 fundamental vibrations divide into:  $12A' + 3A''$  with all modes active in both IR and Raman, the  $A'$  modes being polarized and having  $A/B$  hybrid contours, the  $A''$  modes  $C$ -type contours. From the rotational constants determined by microwave spectroscopy the  $PR$  separations were calculated<sup>13</sup> to be 16, 13 and  $25\text{ cm}^{-1}$  for the  $A$ ,  $B$  and  $C$  bands, respectively.

The infrared and Raman spectra of the liquid are shown in Figs. 1 and 2, respectively, while the wavenumbers of the observed IR and Raman bands are listed in Table 3. As apparent from these data, the assignment is a straightforward matter with

the exception of the intense doublet in the carbonyl stretching region. The relative intensities of these two bands are sensitive to changes in the polarity of the solvent. In the liquid phase the lower band is the most intense, but in a  $\text{CCl}_4$  solution the intensities become almost equal. This shift is most pronounced in the Raman spectra. Further, in the  $\text{CCl}_4$  solution the bands at about  $1800\text{ cm}^{-1}$  split into two close components in both IR and Raman. We have no ready explanation for this effect. In the vapour phase the ratio of extinction between the bands at 1826 and  $1745\text{ cm}^{-1}$  is drastically reversed:  $\epsilon_{1826}/\epsilon_{1745} \sim 4.5$ .

Similar effects occur in a large number of carbonyl compounds, such as unsaturated  $\gamma$ -lactones,<sup>14</sup> and

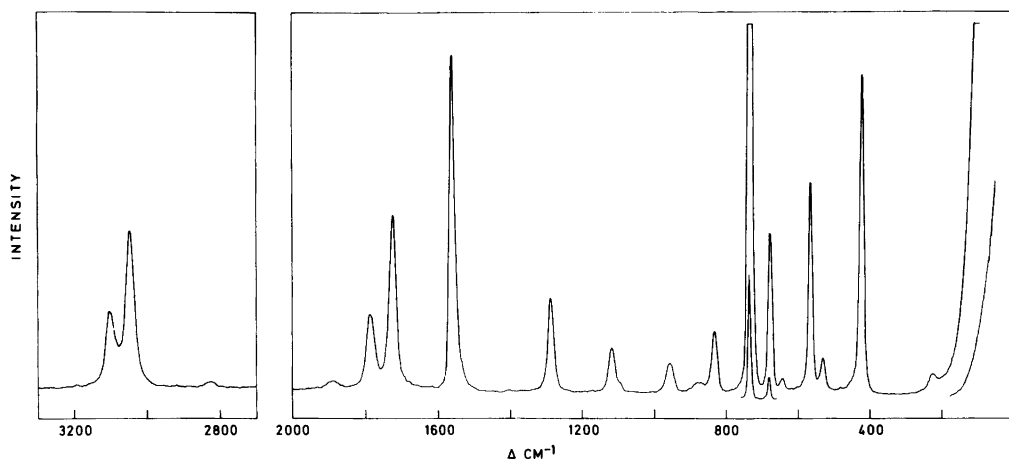


Fig. 2. Raman spectrum of 1,3,4-oxathiazol-2-one in the liquid phase.

Table 3. Infrared and Raman spectral data for 1,3,4-oxathiazol-2-one.

Infrared <sup>a</sup>			Raman <sup>a</sup>			Assignment
CCl <sub>4</sub> solution	Vapour	Liquid	Amorphous solid-180°	CCl <sub>4</sub> solution	Liquid	
		3950 w <sup>b</sup>				$\nu_1 + \nu_{12}$
		3650 w				$\nu_1 + \nu_{10}$
3610		3610 w				$\nu_1 + \nu_{14}$
3535		3528 w				$2 \times \nu_2$
3470		3475 w				$\nu_2 + \nu_6 + \nu_7$
		3370 w				$\nu_2 + \nu_3$
3146		3143 m	3143	3145	3144 m P	$2 \times \nu_3$
3089		3086 s	3073	3088	3088 s P	$\nu_1$
1956		1955 w sh				comb.
1889	1896 } 1889 } 1880 } 1833 }	A/B 1908 m	1923		1904 vw	$2 \times \nu_6$
1810	1826 } 1817 }	A/B 1809 vs	1812	1807	1806 m P	$\nu_2$
1803	1751 }			1801		FR
1745	1745 } 1735 }	A/B 1747 vs	1743	1746	1740 s P	$\nu_6 + \nu_7$
		1663 m	1680			comb.
1577	1587 } 1581 } 1574 }	A/B 1576 vs	1573	1578	1573 s P	$\nu_3$
		1540 w sh				comb.
		1516 w				comb.
		1464 w				comb.
		1409 w				$\nu_8 + \nu_9$
		1380 w				comb.
1293	1303 } 1294 } 1287 }	A/B 1297 m	1298	1295	1297 m P	$\nu_4$
1173		1256 w				comb.
1157		1175 w	1180			comb.
		1157 w sh	1163			comb.
1128	1144 } 1136 } 1127 }	A/B 1124 vs	1123	1127	1124 w P	$\nu_5$
1096		1101 w sh	1108		1102 vw	comb.
1059		1061 w	1070			$\nu_{11} + \nu_{13}$
948	952 } 946 } 939 }	A/B 958 vs	966	955	959 w P	$\nu_6$
868	878 } 867 } 852 }	C 879 m	888		878 vw D	$\nu_{12}$
823	824 } 812 }	833 s	840	827	835 w P	$\nu_7$
		792 w				impurity
	741 } 734 } 726 }	A/B 734	736	735	737 vs P	$\nu_8$
677		680 w	686	679	681 s P	$\nu_9$

Table 3. Continued.

643	656 } 643 } 632 }	C	643	645	646 vw D	$\nu_{13}$	
			626 w sh	627		$\nu_{11} + \nu_{15}$	
565	569 } 562 } 556 }	A/B	566 s	568	567	570 s P	$\nu_{10}$
531	544 } 529 } 516 }	C	529 s	532	534	532 w D	$\nu_{14}$
421			422 m	425	424	426 s P	$\nu_{11}$
214			212 <sup>c</sup> m	232		223 vw D	$\nu_{15}$

<sup>a</sup> The weak infrared and Raman bands in the regions 5000–4000 and 3000–2000  $\text{cm}^{-1}$  are omitted. <sup>b</sup> w, weak; m, medium; s, strong; v, very; sh, shoulder; P, polarized; D, depolarized; FR, Fermi resonance. <sup>c</sup> In cyclohexane solution.

it is assumed that this behaviour is caused by Fermi resonance between  $\nu_2$  and the combination band  $\nu_6 + \nu_7$ . It may be noticed that the same changes in intensities are observed with the overtone bands at 3528 and 3475  $\text{cm}^{-1}$ .

## STRUCTURE DETERMINATION AND RESULTS

The molecular electron-diffraction intensities for each of the three camera distances are shown in Fig. 3, and the data ranges and the weight schemes

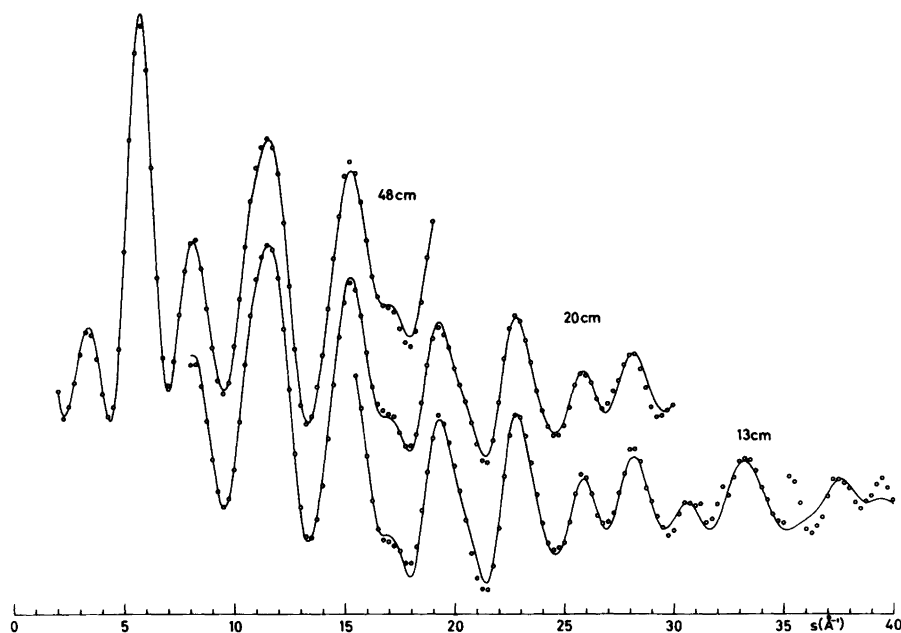


Fig. 3. Observed molecular intensity data (o) for 1,3,4-oxathiazol-2-one obtained from electron-diffraction experiments at three camera distances, compared to calculated intensities (full line) from parameter values given in Table 6a, IIIB.

Table 4. Ranges and weighting of the electron-diffraction data used in the structure refinements.

Curve (camera dist.)	Data range		Data interval	Constants of the weighting schemes <sup>a</sup>						
	$s_{\min}$	$s_{\max}$	$\Delta s$	$s_1$	$s_2$	$w_1$	$w_2$	$p_2$	$p_3$	$W$
48 cm	2.00	19.00	0.125	2.25	19.00	0.1	0.1	-0.64	0.146	1.0
20 cm	8.00	30.00	0.250	8.00	29.00	0.1	0.1	-0.60	0.125	1.0
13 cm	15.50	45.00	0.250	15.50	35.00	0.1	0.1	-0.57	0.100	1.0

<sup>a</sup> See Refs. 6 and 15 for the meaning of the symbols. For diagonal weight matrices  $p_2 = p_3 = 0$ .

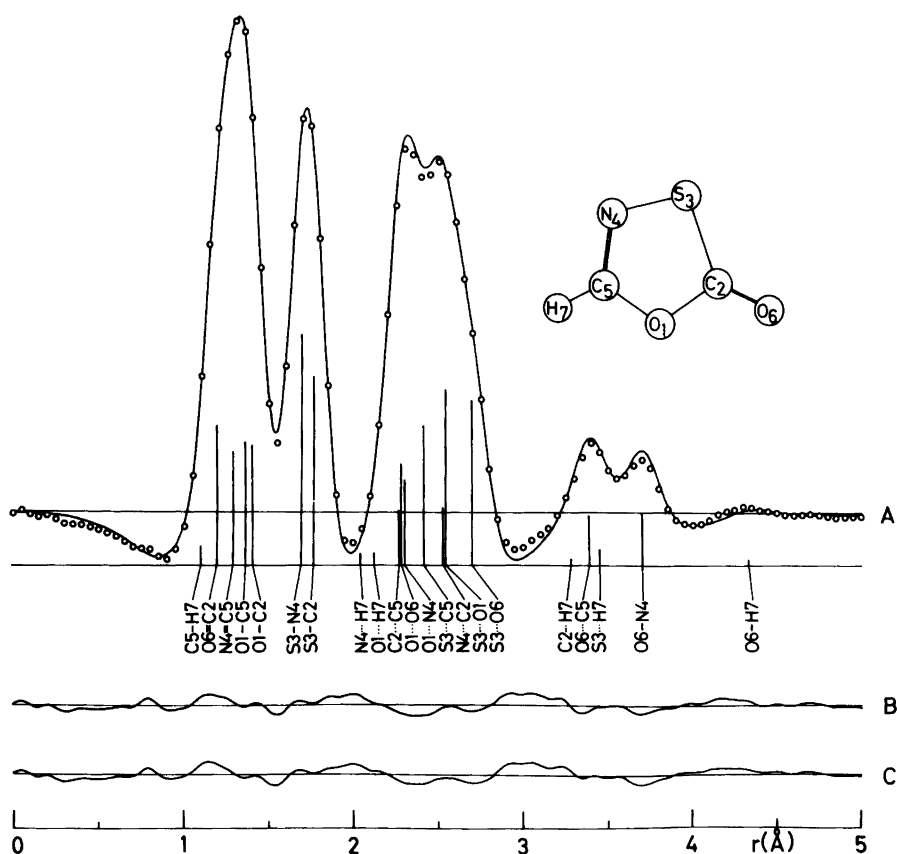


Fig. 4. (A) Experimental radial distribution curve (o) for 1,3,4-oxathiazol-2-one calculated from the intensity data given in Fig. 3 using an artificial damping constant of  $k=0.0020 \text{ \AA}^2$ , and the calculated counterpart (full line) based on the parameter values of Table 6a, IIIB; (B) the corresponding difference curve; and (C) the difference curve using parameter values of Table 6a, IIIC.

A molecular model with numbering of the atoms is shown and the vertical lines indicate the positions of the interatomic distances.

used in the structure analysis are summarized in Table 4.

From the experimental modified molecular intensity curves shown in Fig. 3 a composite curve was computed by scaling and averaging intensity values in the overlap regions. In Fig. 4 the radial distribution curve calculated from this connected curve is presented together with a molecular model. The line diagram under the curve gives the positions and the relative weights of the 21 different interatomic distances of the molecule according to one of the final models. The line diagram demonstrates the high degree of distance overlap and also the discouraging expectation of a conventional approach refining all the 32 geometrical and vibrational parameters together. An attempt to refine a few of the  $u$ -values together with the geometrical parameters demonstrated this quite clearly. On the other hand the geometric parameters refined normally in a few cycles if assumed  $u$ -values were kept constant.

In order to determine the geometrical parameters with confidence, it is of course important to obtain

as reliable  $u$ -values as possible. Further, in order to test the influence of the chosen set of  $u$ -values on the geometrical parameters it was judged useful to try several independently obtained sets. Three such sets were used as given in Table 5. The first set (I) is composed of values simply assumed by one of us (L.F.) based upon many years of experience and analogy to other compounds with similar structure features. The second set (II) was computed from an estimated force field with a diagonal F matrix in terms of valence coordinates including redundancies. Force constant values were estimated with the aid of previous normal coordinate analyses of related molecules: maleic anhydride,<sup>16,17</sup> furan<sup>18</sup> and different diazoles.<sup>18</sup> The third set of  $u$ -values (III) was obtained together with the perpendicular amplitude correction coefficients ( $K$ -values) from a force field adjusted so as to give a fair fit to the observed fundamental frequencies and reproduce sign and magnitude of the centrifugal distortion constants and the inertial defect.

Several preliminary refinement approaches were tried including the assumption of unplanarity and

Table 5. Vibrational amplitude quantities in Å for 1,3,4-oxathiazol-2-one. I, II and III refer, respectively, to assumed values, values computed from an assumed force field and values calculated from a force field adjusted to fit the observed fundamental frequencies as described in the text. The subscripts T and 0 refer to the temperatures 328 K and 0 K, respectively.

	I	II	III	$K_T$	$u_0$	$K_0$
	$u$	$u_T$	$u_T$			
O1-C2	0.045	0.045	0.0471	0.00246	0.0461	0.00211
O1-C5	0.045	0.045	0.0473	0.00433	0.0465	0.00269
S3-C2	0.050	0.043	0.0502	0.00136	0.0471	0.00117
S3-N4	0.050	0.044	0.0541	0.00275	0.0505	0.00169
N4=C5	0.040	0.045	0.0417	0.00250	0.0416	0.00219
O6=C2	0.039	0.039	0.0377	0.00641	0.0375	0.00387
C5-H7	0.074	0.077	0.0767	0.02522	0.0767	0.02099
S3...O1	0.056	0.046	0.0561	0.00078	0.0513	0.00053
N4...C2	0.056	0.051	0.0606	0.00236	0.0564	0.00145
S3...C5	0.050	0.048	0.0564	0.00115	0.0520	0.00078
O1...N4	0.050	0.049	0.0532	0.00335	0.0515	0.00180
C2...C5	0.055	0.051	0.0576	0.00198	0.0545	0.00141
O1...O6	0.057	0.057	0.0582	0.00400	0.0541	0.00204
S3...O6	0.058	0.055	0.0612	0.00176	0.0540	0.00093
O1...H7	0.099	0.101	0.0999	0.01715	0.0992	0.01226
N4...H7	0.077	0.101	0.0972	0.01452	0.0968	0.01186
O6...N4	0.080	0.055	0.0638	0.00044	0.0584	0.00036
O6...C5	0.066	0.057	0.0615	0.00070	0.0571	0.00052
S3...H7	0.090	0.090	0.0940	0.00871	0.0912	0.00662
C2...H7	0.090	0.093	0.0957	0.00996	0.0939	0.00750
O6...H7	0.090	0.102	0.1031	0.00580	0.0999	0.00482

Table 6a. Bond distances ( $r_a$ -values in Å) and valence angles (in degrees) for 1,3,4-oxathiazol-2-one obtained in structural refinement of planar models by the method of least squares based upon electron-diffraction data alone (ED) or combined with data from microwave spectroscopy (ED&MW). The  $R$ -values express the quality of fit for the electron-diffraction data ( $R = \sum w_i(I_{\text{obs}} - I_{\text{calc}})^2 / \sum w_i I_{\text{obs}}^2$ ). I, II and III refer to the set of values for the vibrational parameters used (See Table 3). The meaning of  $r_a$ ,  $r_x$ ,  $r_x^\circ$  and  $r_z$  is described in the text.

	I(ED) $r_a$ -model	II(ED) $r_a$ -model	IIIA(ED) $r_a$ -model	IIIB(ED) $r_x$ -model	IIIC(ED&MW) $r_x^\circ$ -model
$r(\text{O1}-\text{C2})$	1.398(3)	1.395(4)	1.398(4)	1.399(4)	1.402(3)
$r(\text{O1}-\text{C5})$	1.356(3)	1.355(4)	1.356(3)	1.356(3)	1.356(3)
$r(\text{S3}-\text{C2})$	1.769(2)	1.772(2)	1.765(2)	1.766(2)	1.767(2)
$r(\text{S3}-\text{N4})$	1.690(2)	1.687(1)	1.690(2)	1.690(2)	1.690(2)
$r(\text{N4}=\text{C5})$	1.280(3)	1.280(3)	1.283(3)	1.284(3)	1.286(2)
$r(\text{O6}=\text{C2})$	1.189(2)	1.192(2)	1.191(2)	1.191(2)	1.192(2)
$r(\text{CS}-\text{H7})$	1.095-	1.095-	1.095-	1.095-	1.102(19)
$\angle \text{C5O1C2}$	110.7(2)	110.7(2)	110.8(2)	110.9(2)	110.8(2)
$\angle \text{O1C2O6}$	122.9(3)	123.5(3)	122.7(3)	122.7(3)	122.6(3)
$\angle \text{C2S3N4}$	93.6(1)	93.5(1)	93.8(1)	93.8(1)	93.8(1)
$\angle \text{O1C5H7}$	120.0-	120.0-	120.0-	120.0-	114.5(31)
$\angle \text{O1C2S3, dep.}$	106.4	106.4	106.4	106.2	106.3
$\angle \text{O1C5N4, dep.}$	121.2	121.2	121.1	121.3	121.1
$\angle \text{C5N4S3, dep.}$	108.0	108.0	107.9	107.9	107.9
$R (\%)$	9.86	9.58	9.92	9.94	9.91

Table 6b. Rotational constants ( $A$ ,  $B$ ,  $C$  in MHz) calculated from models given above, and in square brackets the values obtained from the microwave study expressed in terms of the operational parameter  $r_0$ .

	I( $r_a$ )	II( $r_a$ )	IIIA( $r_a$ )	IIIB( $r_x$ )	IIIC( $r_x^\circ$ )
$A_0 [5587.411(11)]$	5594.8(174)	5595.0(163)	5603.0(178)	5613.7(177)	5582.6(13)
$B_0 [3645.873(9)]$	3638.6(41)	3639.6(37)	3636.7(41)	3643.7(41)	3643.8(4)
$C_0 [2205.464(9)]$	2204.7(25)	2205.1(25)	2205.3(26)	2209.6(26)	2204.7(2)

Table 6c. Rotational constants corresponding to distances between mean positions of atoms in ground vibrational state, *i.e.* the comparable quantities  $r_z^\circ$  for electron-diffraction and  $r_z$  for microwave results.

	I	II	IIIA	IIIB	IIIC
$A_z [5582.0(16)]$	5604.8(174)	5605.2(163)	5613.2(178)	5611.2(177)	5582.6(13)
$B_z [3643.5(7)]$	3646.8(41)	3647.9(37)	3645.1(41)	3639.7(41)	3643.8(4)
$C_z [2204.8(2)]$	2209.3(25)	2209.8(25)	2210.0(26)	2207.7(26)	2204.7(2)

the assumption that the two ring C–O distances were equal. The first assumption led to the conclusion that a possible deviation from planarity had to be very small, in accordance with the microwave data unambiguously demonstrating the

planarity. The second assumption seemed not necessary since the  $\text{O}_1-\text{C}_2$  distance repeatedly refined to be about 0.05 Å larger than the  $\text{O}_1-\text{C}_5$  distance, even for refinements where the distances had the reverse relative magnitude for the start



model. In attempts to refine  $r(\text{C}-\text{H})$  and  $\angle \text{O1C5H7}$  rather large oscillations were encountered and the position of the hydrogen atom was therefore kept constant. The results of three refinements (I, II and III A) using the corresponding three sets of  $u$ -values given in Table 5, are presented in Table 6a. Only the independent distance parameters are given while both independent and dependent angle values are listed. In these refinements shrinkage effects were neglected. In refinement III B (see Table 6a) shrinkage effects were accounted for using the  $u_{\text{T}}$ - and  $K_{\text{T}}$ -values of Table 5 (III) and the relation<sup>19,20</sup>

$$r_{\text{a}} = r_{\text{x}} - u_{\text{T}}^2/r_{\text{a}} + K_{\text{T}} \quad (1)$$

to obtain the geometrically inconsistent set of  $r_{\text{a}}$  values from the geometrically consistent set of  $r_{\text{x}}$ -values (*i.e.*  $r_{\text{x}}$ -model). In each of the four refinements the rotational constants were computed from the distance and angle parameters describing the geometry of the molecule, *i.e.* based on  $r_{\text{a}}$ -values for refinements I, II and III A and on  $r_{\text{x}}$ -values for refinement III B. The results are compared with the values based upon  $r_{\text{o}}$ -parameters obtained from the microwave study in Table 6b. The refinements were carried out both using diagonal and non-diagonal weight matrices (see Table 4). The actual parameter values given are obtained using diagonal weight matrices, while the standard deviations given in parentheses are obtained with non-diagonal weight matrices. Comparisons of the standard deviations obtained for the two types of weight matrices showed that correlation among the data could be accounted for by applying factors of 1.5–2.0 to the standard deviations obtained in refinements with diagonal weight matrices. The standard deviations given in Tables 6a–c do not include estimates of the uncertainty in the  $s$ -scale (0.1% in the electron wavelength) which corresponds to 0.1% for the distance parameters and about 0.2% for the rotational constants.

The good correspondence between the values of the refinements I to III A given in Table 6 may be interpreted as a demonstration of the insensitivity of the geometrical parameters to the choice of  $u$ -values. However, other less carefully chosen sets of  $u$ -values were also tried with considerably less success. Comparisons of the results of refinements III A and III B show that the effect of neglecting shrinkage effects is small. However, the relatively large differences in the computed rotational con-

stants for these two refinements as compared to the small shifts in the parameter values for the bond distances and valence angles, reflect the fact that the calculations are based upon two different types of distance parameters, namely  $r_{\text{a}}$  and  $r_{\text{x}}$  for refinements IIIA and IIIB, respectively. The rotational constants originating from the electron-diffraction data are not significantly different from the microwave values even in comparisons on the  $r_{\text{a}}$  to  $r_{\text{o}}$  and  $r_{\text{x}}$  to  $r_{\text{o}}$  level, and the results of the two investigations seem to be consistent. The results appear to indicate that the error introduced by such comparisons is small since both the  $r_{\text{a}}$  and  $r_{\text{x}}$  distances should be longer than  $r_{\text{o}}$  resulting in systematically lower values for the corresponding rotational constants, whereas the rotational constants from the two methods (Table 6b) do not show such systematic discrepancies. For the same reason scale problems appear to be ruled out. However, one should note the effect of the fixed hydrogen position. The rotational constants obtained in a refinement corresponding to III B for  $\angle \text{O1C5H7} = 115^\circ$  were, for example, all found to be larger than the corresponding microwave values. This change also caused an improved least-squares fit to the electron-diffraction data ( $R = 9.79\%$ ).

To provide a better basis for comparisons of the results and to attempt conjoint refinements based on information from both methods, the rotational constants were corrected so as to be expressed in terms of distances corresponding to the mean positions of the atoms in the ground vibrational state, which are denoted  $r_{\text{x}}$  and  $r_{\text{x}}^0$  when derived from microwave and electron-diffraction data, respectively. The necessary correction terms were computed from the force field used to calculate  $u$ -value set III. For the microwave rotational constants centrifugal corrections and electronic contributions were neglected giving  $B_{\text{x}} - B_0 \approx \delta B_{\text{vib}}$  where the vibrational corrections,  $\delta B_{\text{vib}}$ , require only harmonic force constants.<sup>19,20</sup> The corrected values are given in Table 6c, and the estimated standard deviations ( $\sigma_{\text{x}}$ ) are taken to be 30% of the  $\delta B_{\text{vib}}$  correction terms. For the electron-diffraction rotational constants the following relation was used in addition to Eqn. 1,<sup>19,20</sup>

$$r_{\text{x}}^0 = r_{\text{x}} + (K_{\text{T}} - K_0) - \frac{3}{2}a_3(u_{\text{T}}^2 - u_0^2) \quad (2)$$

where  $K_0$  and  $u_0$  refer to 0 K (See Table 5).  $a_3$  is an anharmonicity constant assumed to be 0 and  $2 \text{ \AA}^{-1}$

for nonbonded interactions and for bond distances, respectively.<sup>20</sup> The rotational constants expressed by  $r_x^0$  parameters calculated from the  $r_x$ -values of Table 6a are given in Table 6c for the four refinements, I, II, III A and III B. The standard deviations do not include uncertainties in the applied correction terms.

A structure based on  $r_x^0$ -parameters is, like the  $r_x$ -model, corrected for shrinkage. In comparative refinements based on  $r_x$  and  $r_x^0$ -models, the respective angle parameters<sup>21</sup> were found to be nearly equal, the largest difference between  $\angle_x$  and  $\angle_x^0$  being  $0.09^\circ$ . In the  $r_x^0$ -refinement the rotational constants were directly calculated from  $r_x^0$ -parameters, and the rotational constants  $A_z$ ,  $B_z$  and  $C_z$  could be included together with the electron-diffraction data in the least-squares refinement of the structure.<sup>20</sup> The observed rotational constants were given relative weights according to their estimated standard deviations ( $\sigma_z^{-2}$ ), and the data originating from the two methods were weighted so as to give standard deviations for the  $r_x^0$  rotational constants within the values for the corresponding  $\sigma_z$ -estimates. Using the model with fixed hydrogen position, such requirements were obtained for a model which gave a least-squares fit to the electron-diffraction data of  $R=10.06\%$ . In the combined analysis including variation of the hydrogen position convergence was obtained also for  $r(\text{C5-H7})$  and  $\angle \text{O1C5H7}$ . For fixed C-H distance ( $1.095 \text{ \AA}$ ) the hydrogen angle parameter refined to  $114.8(3.1)^\circ$ . The final result of the combined refinement of the structure is given in Table 6 a (III C). The refinement of the hydrogen position did not significantly affect the determination of the other geometrical parameters. The larger elements of the correlation matrix ( $|\rho| > 0.6$ ) are  $\rho(r(\text{O1C2}), r(\text{O1C5})) = -0.73$  and  $\rho(\angle \text{C2S3N4}, \angle \text{O1C5H7}) = -0.72$ . The standard deviations given are obtained using diagonal weight matrices and factors to account for correlation among the electron-diffraction data as established by previous refinements.

The molecular intensities and radial distributions calculated from the parameter values of III B, Table 5, are shown in Figs. 3 and 4, respectively, together with the experimental counterparts. The differences between experimental and calculated radial distribution curves are included in Fig. 4 for parameter set III B as well as for III C.

## DISCUSSION

The consistency in the geometrical parameters obtained using three different sets of fixed  $u$ -values (see Table 6a, refinements I, II, and IIIA) is satisfactory. Provided the existence of data from which reasonable estimates of  $u$ -values or force constants may be made, this demonstrates that electron-diffraction results for molecules with complex distance overlaps may not be as dubious as one could fear. In the present case the electron-diffraction results could also be controlled against the experimental spectroscopic rotational constants and the comparison was gratifying for all three sets of parameter values (Table 6b). The vibrational spectroscopic results provided data for a normal coordinate analysis which gave the  $u$ -value set III and various correction terms needed for comparison on a higher level of confidence (Table 6c) and the final structure determination could be based on the electron-diffraction intensity data in combination with the experimental spectroscopic rotational constants. The results of such a refinement (IIIC of Table 6) represent our final structural parameters. It is seen that this combined approach led to determination of the hydrogen position which had to be assumed in the previous refinements. The difference curves of Fig. 4 and the obtained  $R$ -factors show the good correspondence with the microwave data since no significant loss in the agreement between experimental and calculated curves was encountered when the parameters were adjusted so as to give a good fit to the microwave rotational constants.

The established planarity of the molecule is naturally related to  $\pi$ -electron delocalization. However, 1,3,4-oxathiazol-2-one pyrolyzes fast at  $500^\circ\text{C}$ , furan slowly at  $1000^\circ\text{C}$ , while benzene is stable even at  $1150^\circ\text{C}$ , all on a quartz surface under low-pressure conditions ( $20\text{--}30 \text{ mTorr}$ ).<sup>21</sup> It is therefore tentatively suggested that  $\pi$ -type orbitals of 1,3,4-oxathiazol-2-one are of less importance for maintaining molecular planarity than corresponding orbitals in furan. Comparisons of bond lengths should also yield some information about the degree of delocalization, although effects due to variations in hybridization of the atoms involved and differences in adjacent atoms may obscure the conclusions from such comparisons. Fig. 5 shows the bond lengths of 1,3,4-oxathiazol-2-one and of some related five-membered ring compounds 1–6. Within the experimental error, these are all found to be planar in gas phase.<sup>22–27</sup> Varying numbers and

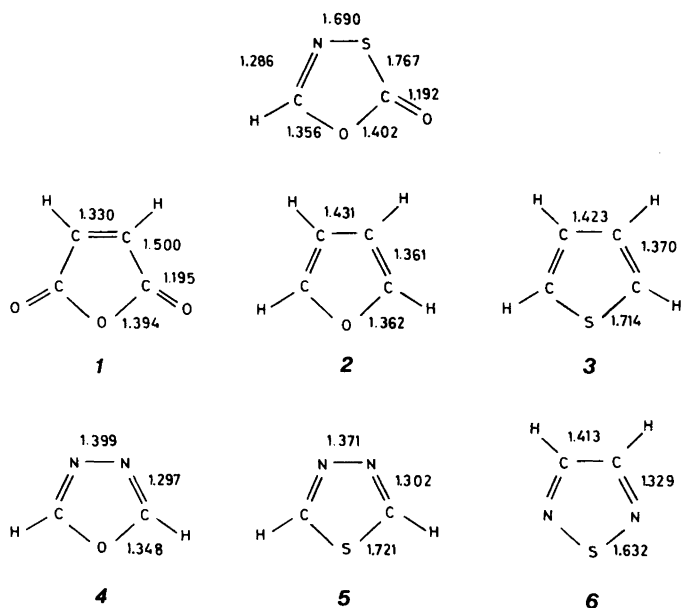


Fig. 5. Bond lengths (in Å) for 1,3,4-oxathiazol-2-one ( $r_a$ -values) and of some related compounds as obtained in electron-diffraction ( $r_e$ -values) and microwave ( $r_s$ -values) investigations: 1 maleic anhydride<sup>22</sup> ( $r_e$ ), 2 furan<sup>23</sup> ( $r_s$ ), 3 thiophene<sup>24</sup> ( $r_s$ ), 4 1,3,4-oxadiazole<sup>25</sup> ( $r_s$ ), 5 1,3,4-thiadiazole<sup>26</sup> ( $r_s$ ) and 6 1,2,5-thiadiazole<sup>27</sup> ( $r_e$ ).

types of heteroatoms have caused variations in the angle deformations needed for ring closure throughout this series. In 1,3,4-oxathiazol-2-one the C–H and C=O bonds are tilted approximately the same amount towards the oxygen atom from the bisectors of the corresponding ring angles, as the corresponding bonds in 1 and 4. The difference in lengths of the two types of O–C( $sp^2$ ) bonds,  $r(\text{O}–\text{C}(=\text{O})) = 1.402$  Å and  $r(\text{O}–\text{C}(=\text{N})) = 1.356$  Å, may be seen as a consequence of the difference in electronegativity of the neighbouring oxygen and nitrogen atoms, and the result is consistent with the values of 1.394 and 1.348 Å, respectively, for the corresponding bonds in 1 and 4. The length of the C=O bond (1.192 Å) suggests, as for 1, that the carbonyl  $\pi$ -electrons do not participate in delocalization of the  $\pi$ -electron system. As compared to the N=C bonds of 4–6 the N=C bond of 1.286 Å in 1,3,4-oxathiazol-2-one is short, and it approaches the value of 1.277(2) Å in formaldazine<sup>28</sup> ( $\text{H}_2\text{C}=\text{N}–\text{N}=\text{CH}_2$ ) for which the antiperiplanar conformer is the more stable, and the N–N bond of 1.418(3) Å is longer than the corresponding bonds of 4 and 5. The described shortening of the N=C bond is

consistent with the lengthening of the two adjacent bonds C–O and N–S as compared to the C–O bond in 4 and the N–S bond in 6. Also the S–C( $sp^2$ ) bond of 1.767 Å is long compared to the corresponding bonds of 1.714 Å in 3 and 1.721 Å in 5, and it is found to be closer to the values of 1.747(3) Å and 1.777(4) Å of methylvinylsulfide<sup>29</sup> ( $\text{H}_2\text{C}=\text{CHSCH}_3$ ) and dimethyldithiocarbonate<sup>30</sup> ( $\text{O}=\text{C}(\text{SCH}_3)_2$ ), respectively. The neighbouring strongly electronegative oxygen may be responsible for part of the described lengthening of the S–C( $sp^2$ ) bond as it was suggested for the O–C( $sp^2$ ) bond of 1.402 Å. Assuming that the  $\sigma$  bond lengths are more or less the same for corresponding atom pairs in the different compounds, this qualitative discussion of the structural results for 1,3,4-oxathiazol-2-one suggests that  $\pi$ -electron delocalization is less pronounced in this compound than in compounds 2–6, which supports the tentative conclusion from the pyrolysis experiments.<sup>21</sup>

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