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The Molecular Structure of Gaseous 5-Methyl-1,3,4-oxathiazole-2-one, $CH_3C{=}N{-}S{-}CO{-}O$

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The title compound has been studied by microwave, infrared and Raman spectroscopy and by electron diffraction from the vapour. The spectral data have been interpreted in terms of C_s-symmetry, and a normal coordinate analysis has been carried out. The final structural refinement was based upon electron-diffraction intensities in combination with the microwave rotational constants. The vibrational amplitude parameters applied were derived from force field calculations, which were also used to calculate shrinkage corrections and to make the electron-diffraction and spectroscopic rotational constants compatible. As compared with the structure of 1,3,4-oxathiazol-2-one, the results suggest that methyl substitution has caused only minor changes in the ring geometry. The C(ring)–C (sp^3) bond (r_a) was found to be 1.487(3) Å and the three fold rotational barrier for the methyl group as determined from the microwave data was 5.98 kJ/mol. Due to some inconsistencies in the force-field calculations for the title compound and the parent molecule a recalculation for the latter was included. A new set of amplitude quantities was used in the structural reanalysis, but significant changes in the geometrical parameters were not encountered.

The results of spectroscopic and electron-diffraction studies of 1,3,4-oxathiazol-2-one (I) have recently been published.[1] The investigation was carried out in order to provide a basis for a future theoretical treatment of its facile pyrolysis. The methyl derivative, 5-methyl-1,3,4-oxathiazol-2-one (II), starts to break down at about 600K on a quartz surface under low pressure[2] and thus exhibits similar pyrolysis properties as the parent molecule (I). Comparable structural information was wanted for I and II, and this paper reports results for II as obtained by microwave, infrared and Raman spectroscopy and by electron-diffraction.

EXPERIMENTAL

(a) Sample. 5-Methyl-1,3,4-oxathiazole-2-one was prepared as described elsewhere.[3] None of the recorded infrared, Raman or microwave spectra indicated the presence of impurities.

(b) Microwave. Microwave spectra were recorded at 10–50 mTorr and at room temperature in the 12.5–40 GHz regions using a Hewlett-Packard 8460 MRR instrument. Stark voltages in the range 25–2000 V/cm were applied.

(c) Infrared and Raman. Infrared spectra of the vapour (pathlength 1 m), the CCl_4 and CS_2 solutions, the pure liquid and of the unannealed and annealed solid at liquid nitrogen temperature were recorded on a Perkin-Elmer Model 225 spectrometer and with a fast scan Bruker Model 114C interferometer. Far infrared spectra of cyclohexane solutions were obtained with the Bruker interferometer over the region 400–50 cm^{-1}.

Raman spectra were obtained on a modified[4] 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[5] for nozzle-to-plate distances of 479.30 and 199.30 mm, using Kodac Electron Image plates and a nozzle-tip temperature of 62 °C. The electron wavelength was 0.06469 Å as calibrated against diffraction patterns

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of gaseous benzene. The estimated standard deviation in the determination of the electron wavelength is 0.1 %. Three, respectively, four plates for the long (48 cm) and the short (20 cm) camera distances were selected for the structure analysis. The plates were densitometered while oscillating the plates and the obtained densities were processed[6] using a blackness correction of $1+0.03D+0.09D^2+0.03D^3$. A modification function $s/|f'_C|\cdot|f'_S|$ was applied and a computer program, essentially equal to that described by L. Hedberg,[7] was used to subtract the background on the modified form employing polynomia of 9th degree. The various atomic scattering amplitudes and phases[6] were calculated as described for the parent molecule.[1]

ANALYSIS OF MICROWAVE DATA

Rotational and distortion constants. A total of 81 *R*-type μ_a-lines ($3<J<13$) and 3 *Q*-type lines:

$11_{1.11}\rightarrow 11_{1.10}$ at 28340.19 MHz

$14_{3.12}\rightarrow 14_{3.11}$ at 27605.09 MHz

$16_{4.13}\rightarrow 16_{4.12}$ at 27464.76 MHz

were assigned to the ground state by their relative intensities and observed Stark patterns. The three *Q*-type transitions above are reported to introduce as a *sine qua non* that rotational and distortion constants (Table 1) of a molecule should never be published without some experimental frequencies which may be used to identify compounds by searching for authentic transitions. All experimental frequencies are available upon request. The 84 observed lines were fitted by the least squares method (r.m.s. deviation 0.07 MHz). One of the distortion constants, Δ_K, had virtually no influence on the frequencies. It was hence constrained to 1.025 kHz as calculated from a force field. This approach affected the determination of the remaining distortion constants and was necessary to give agreement with values obtained in force field calculations.

Line splittings due to the quadrupole moment of nitrogen or to CH_3 tunnelling (*A*,*E*) splitting for the ground state were not observed. The established $ID=I_c-I_b-I_a=3.0987$ uÅ^2 is consistent with a planar heavy atom structure.

Table 1. Rotational ground state parameters for 5-methyl-1,3,4-oxathiazole-2-one. Rotational constants (A_o, B_o, C_o) in MHz. Quartic distortion constants (Δ_J,Δ_{JK},Δ_K,δ_J,δ_{JK}) in kHz. Inertial defect (ID) in uÅ^2 and the asymmetry parameter (κ) dimensionless.[a]

A_o	4239.844 (18)[a]
B_o	2113.2295(28)
C_o	1422.6055(20
κ	−0.5097
ID	−3.0987
Δ_J	0.1161(77)
Δ_{JK}	0.110 (31)
Δ_K	1.025 −[b]
δ_J	0.0224(52)
δ_{JK}	0.218 (84)

[a] Values in parentheses represent one standard deviation. [b] Constrained to value calculated from a force field.

Table 2. Observed transitions (MHz) associated with the first torsionally excited level of 5-methyl-1,3,4-oxathiazole-2-one (ν_A, ν_E) and the corresponding observed and calculated line splittings ($\nu_A-\nu_E$); with the ground vibrational state values ($\nu^\circ_{A,E}$) in square brackets; and the calculated CH_3-torsion hindering barrier, V_3 in cm^{-1}.

Transition	ν_A	ν_E	$\nu_A-\nu_E$		V_3[a]
			Obs.	Calc.	
$4_{2.2}-5_{2.3}$	19245.3	19229.5	15.8	15.3	498.6
	[19257.73]		–	[0.01]	
$5_{2.4}-6_{2.5}$	20581.4	20589.4	−8.0	−7.8	498.7
	[20591.34]		–	[0.05]	
$6_{1.5}-7_{1.6}$	24545.6	24550.8	−5.2	−5.4	501.3
	[24556.37]		–	[0.15]	
$7_{2.5}-8_{2.6}$	30285.2	30289.0	−3.8	−4.0	502.3
	[30302.34]		–	[0.14]	

[a] $V_3=500.2$ cm^{-1} corresponds to a CH_3 torsional frequency of 143 cm^{-1}.

Table 3. Infrared and Raman spectral data[a] for 5-methyl-1,3,4-oxathiazole-2-one.

Infrared						Raman			Assignment
Vapour		Solution	Liquid	Amorphous solid −180°	Polycryst. solid −180°	Liquid	Amorphous solid −180°	Polycryst. solid −180°	
~3570	vw,?	3505 w[b]	3495 w	3490 w,bd	3460 w 3442 w				$2\times\nu_3$
		3235 w	3230 vw	3240 vw	3260 vw				$2\times\nu_4$
		3022 vw	3020 vw	3028 w		3025 m	3025 m 2999 m,sh	3016 m 3001 m	$\nu_4+\nu_5$
		2980 w	2980 vw	2985 w	2984 w	2984 m,D	2982 s	2982 s	ν_{17}
		2936 w	2935 w	2933 w	2930 w	2934 vs,P	2933 vs	2929 vs	ν_1
		2848 w	2850 vw	2850 w	2851 w 2846 w	2847 w,P	2842 w	2843 w	ν_2
		2809 vw	2810 vw		2803 vw				$\nu_5+\nu_6$
		2744 vw	2740 vw		2735 vw	2745 w,P	2739 w	2739 w	$2\times\nu_6$
1945	w,?	1955 w	1959 w	1970 w	1968 m				comb.[c]
1898	m,?	1907 w	1914 w	1925 m	1919 m				comb.
1833 1820	vs,AB	1820 s	1825 m	1836 m,bd	1836 m	1825 w	1833 w,bd	1833 w	ν_3, FR
1775 1766	s,AB	1766 vs	1762 vs	1756 s	1763 s	1755 m,P	1756 m	1753 m	$2\times\nu_{10}$, FR
		1740 s	1743 s	1734 s	1743 s	1741 m,sh,P	1738 m	1744 m 1726 s	$\nu_9+\nu_{11}$, FR
			1719 w,sh	1718 m			1716 w	1716 m	$\nu_8+\nu_{12}$
		1698 w	1698 w	1700 w	1695 w	1697 w	1698 w	1694 w	$\nu_7+\nu_{15}$
		1646 w	1649 w	1655 w	1658 w 1637 w	1648 w,sh	1650 w	1656 w	comb.
1636 1625	s,AB	1623 s	1624 s	1626 s	1632 s	1622 s,P	1624 s	1632 s	ν_4
				1616 w	1619 m 1611 w				
		1600 vw,sh	1603 w,sh		1604 w 1589 m			1587 w	comb.
		1562 w 1482 vw	1562 w 1483 vw	1567 w	1577 w	1561 w			$2\times\nu_{11}$ $\nu_{10}+\nu_{13}$
			1440 m,sh	1439 m,sh	1444 s		1440 w,sh	1440 w	ν_{18}
1450 1443 1437	m,AB	1433 m	1431 m	1430 m	1432 s	1431 m,P	1426 m	1426 s	ν_5

		1389 m	1390 m	1393 w,sh	1427 s 1401 w	1392 w,sh	1403 w,sh		comb., FR
1398 1392 1387	m,AB	1381 m	1380 m	1381 m	1379 m 1376 s	1381 m,P	1379 m	1378 m	ν_6, FR
		1355 vw	1357 vw,sh						$\nu_{11}+\nu_{21}$
1348 1340 1331	w,AB	1340 vw	1339 vw			1338 vw			$\nu_{10}+\nu_{15}$
		1302 w	1304 w	1308 w	1319 w 1311 w	1303 w			$2\times\nu_{21}$, FR
1274 1270 1263	s,AB	1261 s	1259 s	1261 s	1262 s	1259 w	1260 w		ν_7, FR
1244	w,?	1248 m	1248 m	1250 m,sh	1253 s 1249 m	1248 w	1247 w	1251 w	comb., FR
		1231 w,sh	1225w,sh	1230 w,sh	1228 w				
1180	vw,?	1210 vw,sh	1211 vw		1215 w 1207 w				
		1199 vw,sh			1200 vw	1198 w			comb.
		1161 vw	1159 vw						
1118	vw,?	1138 vw 1112 vw 1087 vw	1137 vw 1109 vw	1146 vw	1151 vw				
1048 1044 1038	m,AB	1041 s	1044 s	1050 s 1039 m,sh	1050 s 1045 s 1041 s	1043 m,P	1048 m	1049 m	ν_8, ν_{19}
1002 995 990	m,AB	993 m	997 m	999 s	1000 s 998 s	997 w	997 w	997 w	ν_9
911 905 900	s,AB	912 s	920 s,bd	930 vs,bd	923 vs	919 w,bd	926 w,bd	919 m	ν_{10}
		881 vw 861 vvw,sh 840 vvw 822 vvw	882 vw 864 vvw,sh 846 vvw 818 vvw	862 vvw	900 vw 855 vvw				comb.
791 786 780	w,AB	783 m	785 m	787 s	803 s 796 m	784 m,P	786 m	803 s	ν_{11}
		766 vvw,sh 745 vvw	766 vvw,sh 744 vw	765 vvw 737 vw	765 vw 733 vw				$\nu_{21}+\nu_{23}$ $\nu_{21}+\nu_{24}$

704 691	w,AB	699 w	700 w	702 m	700 m	699vs,P	701 vs	699 vs	ν_{12}
661 652 639	w,C	651 m	651 m	651 s	658 s	650 w,D	652 w	656 w	ν_{20}
		639 vw,sh	638 vw,sh	638 vw	641 vw				
606 603 600	vw,AB	606 w	605 w	607 m	604 m	605 vs,P	608 vs	609 vs	ν_{13}
596		598 w	598 w	596 w	600 m	597 w,sh	597 w,sh	598 w	ν_{21}
562 556 550	w,AB	557 m	555 m	556 m	563 s 550 s	555 s,P	556 vs	561 s 549 s	ν_{14}
		549 vw,sh	547 vw,sh	548 vw,sh	546 m,sh				$\nu_{16}+\nu_{22}$
442 438 432	w,AB	439 m	440 m	443 m	448 m	440 s,P	444 s	448 s	ν_{15}
		302 w	305 w	310 w	312 m 289 m	305 m,D	308 m	312 m 283 w	ν_{22}
		255 m	258 m	272 m	280 s 271 m	258 w	269 w	270 w	ν_{16}
		180 vw				187 w,D			ν_{23}
143[d]									ν_{24}

[a] Bands in the regions 5000 – 3500 and 2700 – 2000 cm^{-1} were omitted. [b] Abbreviations; s, strong; m, medium; w, weak; v, very; bd, broad; P, polarized; D, depolarized; FR, Fermi resonance; A, B and C denote vapour contours. [c] Combination or overtone, used when several possibilities present. [d] From microwave investigation, see text.

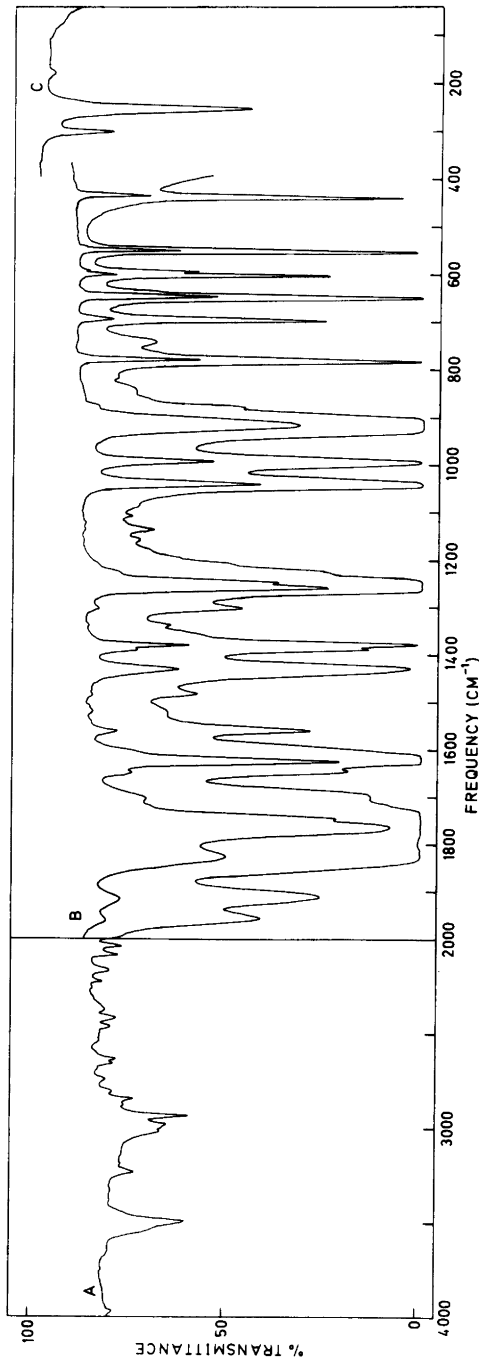

Fig. 1. Infrared spectrum of 5-methyl-1,3,4-oxathiazole-2-one in the liquid phase, (A) 0.025 mm cell and (B) thin film and in cyclohexane solution (C).

Rotational barrier. Transitions associated with the first torsionally excited level are reported in Table 2. Neglecting interference from other vibrational modes, Coriolis coupling *etc.*, and assuming a torsion hindering potential of 3-fold symmetry, $V_3 = 500.2 \pm 1.4$ cm^{-1} (1.43 kcal/mol; 5.98 kJ/mol) reproduces the observed *A,E* splittings within 0.2–0.5 MHz (Table 2). In agreement with our observations for the vibrational ground state, the corresponding calculated $\nu_A^\circ - \nu_E^\circ$ values are too small to be observed with our instrumentation.

VIBRATIONAL SPECTRA

The wavenumbers of the observed bands are listed in Table 3 and the infrared (IR) and Raman spectra of the liquid are shown in Figs. 1 and 2, respectively. The spectra have been interpreted in terms of C_s-symmetry. The 24 fundamental vibrations, divided into 16 *A′* and 8*A″* modes, are all active in both IR and Raman. The A′ modes polarized and have *A,B* hybrid contours, while the *A″* modes exhibit *C*-type contours. The *PR* separations calculated from the rotational constants determined from the rotational spectra[8] were 14, 10 and 21 cm^{-1} for the *A*, *B* and *C* bands, respectively. This is distinctly different from the values of the parent molecule (I).[1]

As apparent from Table 3, the assignment is, with few exceptions, straightforward. Several intense bands are observed in the carbonyl stretching region. The relative intensity of the two strongest infrared bands are reversed going from the vapour phase to the liquid state. Similar effects were observed for the parent molecule,[1] and this behaviour is assumed to be caused by Fermi resonance between ν_3 and a number of combination and overtone bands (Table 3). Except for the lowest *A′* mode, ν_{16}, the remaining *A′* fundamentals have been assigned on basis of the vapour phase contours and the polarization data. The in-plane bending of the methyl group (ν_{16}) has been assigned to an IR band around 255 cm^{-1} for which no vapour phase band contours nor polarization data are available.

Only four of the eight *A″* fundamentals (ν_{17}, ν_{20}, ν_{22} and ν_{23}, Table 3) can readily be assigned on basis of vapour phase band and polarization data. The CH_3 deformation modes, ν_{18} and ν_{19}, were in analogy with 2-methyl-furane[9] assigned to the bands around 1440 and 1041 cm^{-1} with the latter coinciding with ν_8. The weak band at 598 cm^{-1} observed both in IR and Raman was assigned to

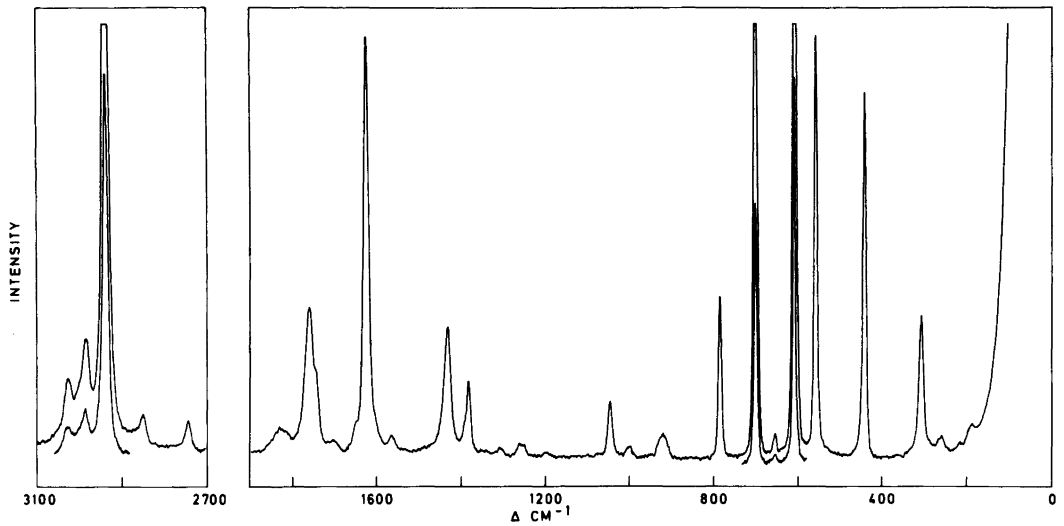

Fig. 2. Raman spectrum of 5-methyl-1,3,4-oxatiazole-2-one in the liquid phase.

the ring deformation, ν_{21}. For the lowest A'' fundamental, the methyl torsional mode, the value of 143 cm^{-1} proposed by the microwave investigation (Table 2), but not observed in the vibrational spectra has been adopted.

FORCE FIELD CALCULATIONS

As for the parent molecule, a force field based on the vibrational spectra data was derived in order to provide possibilities for calculations of vibrational quantities needed in the further structural analysis. A set of initial force constants was based on an estimated force field used for I, augmented with appropriate coordinates for the methyl group accounting for some expected effects from methyl substitution. It was necessary to introduce five additional coordinates in species A' and four in A''. For this purpose the symmetry-adapted combinations of stretchings and bondings were applied, *viz.* $2a_1+3e$, pertaining to local C_{3v} symmetry.[10] In addition one methyl torsion coordinate was introduced. The methyl force constants were thus assumed to be part of a local diagonal F-matrix. The correlations with the symmetry species of C_s, which is the symmetry of the whole molecule, are very simple, *viz.* $5A'(2a_1+3e_a)+4A''(3e_b+c)$. Here c is the ring-methyl coupling, and it is covered by the torsional coordinate. The approximate force field including redundancies, gave calculated frequencies in fair agreement with the observed ones. A set of independent symmetry coordinates was constructed. The secular equation of molecular vibrations was solved in terms of these coordinates. The symmetry force constants were adjusted to fit accurately the experimentally assigned frequencies. This last piece of the analysis was achieved by a method of maintaining the normal-coordinate transformation matrix (L) from the approximate computation.

The final force field was used to calculate root-mean square and perpendicular amplitudes of vibration (u and K-values). The results are given in Table 4 for temperatures of 0 K and 335 K (subscripts O and T, respectively) using atomic coordinates transferred from the parent molecule and describing the methyl group by $\angle OCC=114.5°$ $r(CC)=1.50$ Å, $\angle CCH=109.7°$, $r(CH)=1.09$ Å and $\theta(HCC=N)=0°$. Using the calculated u- and K-values the corrections from r_a to r_α and r_a° were computed as described for I.[1] The force field was also used to compute the vibrational correction terms to the rotational constants (δB_{vib}), and the B_o values were converted to the B_z counterparts neglecting the centrifugal and electronic corrections. The r_z representatives of the rotational constants are given in Table 5, and their standard deviations, σ_z, given in parentheses, are estimated to be 30 % of the calculated δB_{vib} values.

Table 4. Vibrational amplitude quantities in Å for 5-methyl-1,3,4-oxathiazol-2-one calculated from a force field as described in the text at temperatures of 335 and 0 K (subscripts T and 0, respectively).

	u_T	K_T	u_0	K_0
O1–C2	0.0477	0.00425	0.0466	0.00263
O1–C5	0.0478	0.00363	0.0466	0.00250
S3–C2	0.0453	0.00170	0.0436	0.00132
S3–N4	0.0460	0.00321	0.0445	0.00202
N4=C5	0.0458	0.00293	0.0450	0.00246
O6=C2	0.0397	0.00591	0.0392	0.00377
C5–C7	0.0486	0.00730	0.0475	0.00378
C7–H8	0.0790	0.06746	0.0790	0.02901
C7–H9	0.0787	0.07275	0.0787	0.03060
C7–H10	0.0787	0.07275	0.0787	0.03060
S3···O1	0.0489	0.00250	0.0464	0.00116
N4···C2	0.0540	0.00216	0.0517	0.00151
S3···C5	0.0496	0.00182	0.0468	0.00115
O1···N4	0.0549	0.00298	0.0530	0.00175
C2···C5	0.0531	0.00204	0.0509	0.00159
O1···O6	0.0618	0.00591	0.0564	0.00260
S3···O6	0.0580	0.00195	0.0521	0.00101
O1···C7	0.0768	0.00616	0.0642	0.00266
N4···C7	0.0729	0.00415	0.0629	0.00216
O6···N4	0.0588	0.00178	0.0553	0.00088
O6···C5	0.0603	0.00210	0.0558	0.00109
S3···C7	0.0615	0.00107	0.0552	0.00054
C2···C7	0.0694	0.00177	0.0608	0.00101
O6...C7	0.0840	0.00069	0.0681	0.00045
C5···H8	0.1121	0.04089	0.1106	0.01664
C5···H9	0.1118	0.04229	0.1102	0.01729
C5···H10	0.1118	0.04229	0.1102	0.01729
O1···H8	0.1099	0.02891	0.1050	0.01127
O1···H9	0.1974	0.03027	0.1515	0.01217
O1···H10	0.1974	0.03027	0.1515	0.01217
C2···H8	0.1167	0.01817	0.1134	0.00726
C2···H9	0.1716	0.01927	0.1425	0.00766
C2···H10	0.1716	0.01927	0.1425	0.00766
S3···H8	0.1453	0.01875	0.1338	0.00701
S3···H9	0.1406	0.01684	0.1265	0.00662
S3···H10	0.1406	0.01684	0.1265	0.00662
N4···H8	0.1532	0.03292	0.1399	0.01273
N4···H9	0.1617	0.02567	0.1289	0.01063
N4···H10	0.1617	0.02567	0.1289	0.01063
O6···H8	0.1175	0.01230	0.1122	0.00519
O6···H9	0.2131	0.01432	0.1600	0.00564
O6···H10	0.2131	0.01432	0.1600	0.00564
H8···H9	0.1297	0.11626	0.1293	0.04329
H9···H10	0.1297	0.11626	0.1293	0.04329
H8···H10	0.1305	0.12166	0.1302	0.04471

STRUCTURE DETERMINATION

The electron-diffraction intensity data and the corresponding experimental radial distribution curve are shown in Figs. 3 and 4, respectively. The latter figure contains a molecular model with the numbering of the atoms. The geometry is described by the fourteen independent parameters defined in Table 5. In accordance with the results for I and the

Table 5. Structural results[a] for 5-methyl-1,3,4-oxathiazol-2-one obtained in refinements based on electron-diffraction intensities (Fig. 3 and Table 6) in combination with microwave rotational constants[b] (A_z, B_z, C_z) using calculated vibrational parameters (Table 4).

Distances (r_a, Å)	
1. r (O1 – C2)	1.391(6)
2 r (O1 – C5)	1.367(9)
3 r (S3 – C2)	1.768(2)
4 r (S3 – N4)	1.685(2)
5 r (N4 = C5)	1.289(4)
6 r (C2 = O6)	1.198(2)
7 r (C5 – C7)	1.487(3)
8 r (C – H)	1.102(30)
Angles ($\angle_\alpha$, θ_α, degrees)	
9 ∠C5O1C2	111.8(3)
10 ∠O1C2O6	123.6(4)
11 ∠C2S3N4	93.5(2)
12 ∠O1C5C7	115.3(4)
13 ∠CCH	109.6(5)
14 θ(N4C5C7H8)	0. (fixed)
∠O1C2S3	106.4(3)
∠O1C5N4	119.3(2)
∠C5N4S3	109.2(3)
Rotational constants (MHz)[b]	
A [4240.45(18)]	4240.40(18)
B [2112.75(14)]	2112.82(11)
C [1422.53(2)]	1422.55(2)

[a] The independent geometrical parameters are numbered. The correlation coefficients $|\rho(i,j)| > 60\%$ are, $\rho(2,1) = -95$, $\rho(5,1) = +68$, $\rho(5,2) = -75$, $\rho(7,1) = -63$, $\rho(9,2) = -64$, $\rho(12,10) = -77$. Uncertainty in the s-scale (0.1 and 0.2 %, respectively, for r and A, B, C-values) are not included in the estimated standard deviations given in parentheses. [b] Experimental r_z-values in square brackets and r_α°-counterparts are given. Ground state rotational constants in Table 1.

interpretation of the spectral data, the heavy atom skeleton was assumed to be planar. Local C_{3v} symmetry was introduced for the methyl group. The chosen model represented the data well and the constraints were not relaxed.

The vibrational parameters (u-values) were fixed at the calculated values (Table 4), and the geometrical parameters were refined by the least-squares method based on the intensity data using data ranges and diagonal weighting as given in Table 6. The obtained standard deviations were, however, augmented as indicated by comparative refinements using the given diagonal weight matrices and nondiagonal ones with standard values for the off diagonal elements.[11] Shrinkage corrections were implemented by the use of an r_α-model which gave the geometrically inconsistent set of r_a-distances. As for the parent molecule this resulted in insignificant shifts in the refined parameter values. The calculations of the r_α-coordinates were always parallelled by computations of r_α°-coordinates which were simultaneously used to compute the r_α°-representatives of the rotational constants (A_α°, B_α°, C_α°). Thus the structural results obtained from the refinement based on the electron-diffraction data could always be checked against the A_z, B_z and C_z counterparts obtained from the spectroscopic data (Table 5). Such comparisons did not reveal any serious scale problems the A_α°, B_α° and C_α° being 4226(12), 2110(5) and 1420(2) MHz. The final refinement was based on the electron-fiffraction intensities in combination with the experimental rotational constants (A_z, B_z, and C_z) as described previously. The combined approach made it possible to refine the parameter ∠CCH which was previously constrained to 110°. The fitting of the rotational constants is in general accompanied by a poorer fit to the electron-diffraction intensities, which, however, in the present case was insignificant as the pertinent agreement factor changed only from 6.62 to 6.79 %. Consequently, the structural results for the latter refinement (presented in Table 5) are not significantly different from those obtained from the electron-diffraction data alone. The quality of the fit to the electron-diffraction data is also demonstrated by comparisons of calculated intensity and radial distribution curves with the experimental counterparts shown in Figs. 3 and 4, respectively.

As seen from Table 5, the parameter for the conformational orientation of the methyl group, θ(H8C7C5N4) was assigned to 0°. The second conformation ($\theta = 180°$) which gives overall C_s symmetry for the molecule did not give significantly better agreement to the data, the R-factor ratio [$R(180)/R(0)$] being 0.99. Several intermediate orientations were tested, and it was shown that the least-squares fit as well as the remaining geometrical parameters were practically invariant to assumptions regarding this parameter. Therefore, it was not found worthwile to pursue the analysis by including large amplitude treatment for the internal rotor, shown by the interpretation of the microwave data to have a barrier height of 5.98 kJ mol^{-1}.

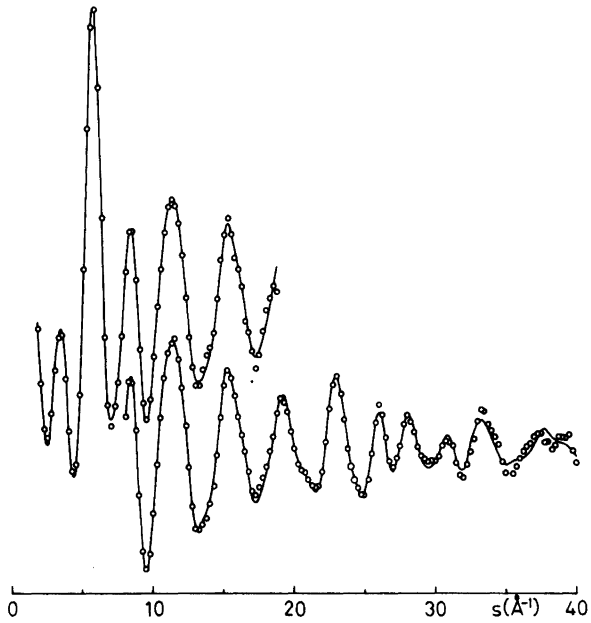

Fig. 3. Observed molecular electron-diffraction intensities (○) 5-methyl-1,3,4-oxathiazole-2-one compared to calculated counterparts (full lines) from parameter values given in Table 5.

DISCUSSION

Comparison of the geometrical parameters of II (Table 5) with those obtained for the parent molecule (I),[1] seems to demonstrate that the effect of the methyl substitution is small, the error limits taken into consideration. On the other hand, there appeared to be some unacceptable deviations in some of the u-values. For example, the u_T-values for the three distances S_3-C_2, S_3-N_4, and $N_4=C_5$ of I were from spectroscopical calculations (third, and final set)[1] found to be 0.0502, 0.0541 and 0.0417 Å, respectively, while the corresponding values for II (Table 4) were 0.0453, 0.0460 and 0.0458 Å. The discrepancies, particularly for the bonds containing sulfur, were too large to be easily rationalized. The close similarity in corresponding geometrical parameter values for I and II probably corroborates the previous conclusion[1] that the molecular geometry is not too sensitive to changes in the u-values, even in these rather difficult cases with severe distance overlap. However, the mentioned discrepancy led to a thorough checking of the normal coordinate calculations for both molecules. Care was taken to base the force fields on transferred force constants from one molecule to the other in the initial set, and to use the same method to adjust the force constants to fit accurately the experimentally assigned frequencies.

For compound II the new vibrational amplitude

Table 6. Data ranges and constants of the weighting schemes[a] used for the electron-diffraction in the structure refinements.

(Camera dist.)	s_{min}	s_{max}	Δs	s_1	s_2	w_1	w_2
48 cm	1.75	18.75	0.125	2.00	18.00	0.1	0.03
20 cm	8.00	40.00	0.250	8.00	40.00	1.0	0.02

[a] See Ref. 6 for definitions of the symbols.

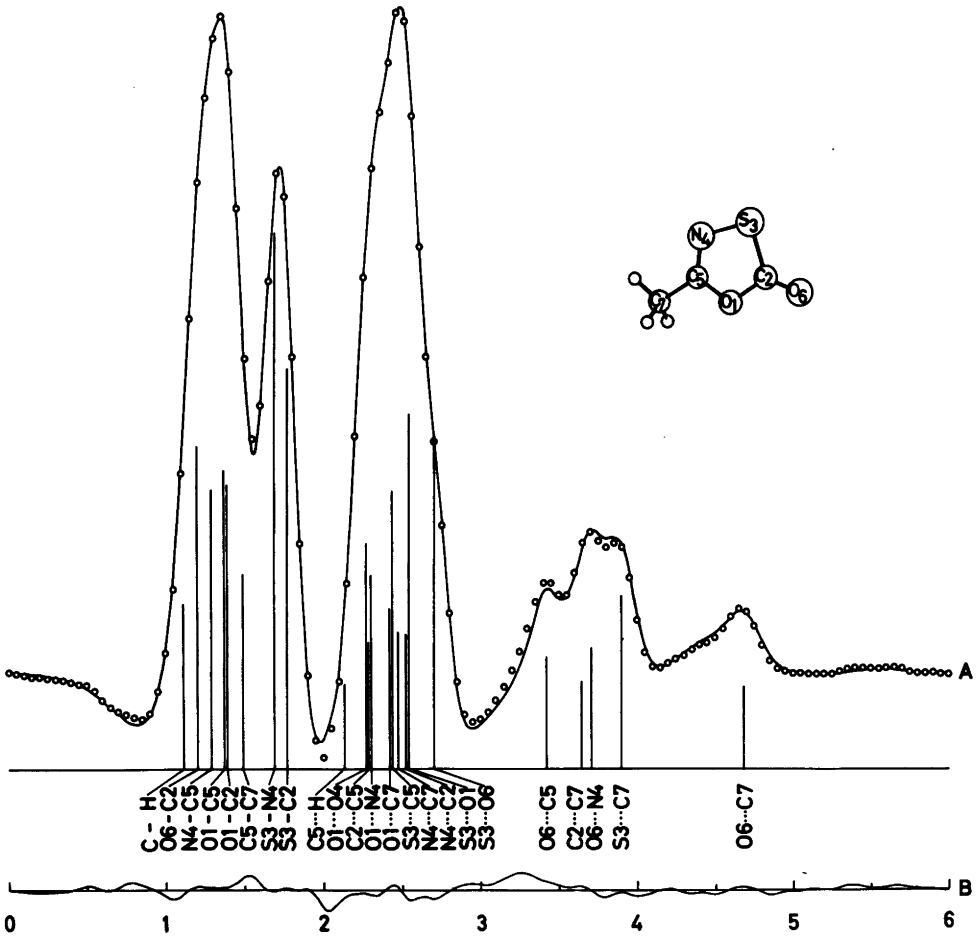

Fig. 4. Experimental radial distribution curve (○) for 5-methyl-1,3,4-oxathiazole-2-one calculated from the intensity data in Fig. 3 using appropriate theoretical intensity values for $s < 1.75$ Å and an artificial damping constant of $k = 0.0020$ Å^2, the calculated counterpart (full line), and the corresponding difference curve. The vertical lines indicate the positions of the interatomic distances, and the numbering of the atoms are given on the inserted model of the molecule.

quantities showed only small deviations from the values given in Table 4. In spite of this the electron-diffraction refinements and the combined electron-diffraction microwave refinements were repeated. None of the new geometrical parameters thus obtained deviate as much as one standard deviation from the data presented in Table 5. A possible influence on the torsion of the methyl group was also tested with no significant changes.

For the parent substance the new set of u-values deviates from that earlier used in the final structural refinement.[1] The new and the old set of u_T-values are presented in Table 7. All the refinements carried out earlier with the old set[1] have been repeated using the new set. The earlier and the new set of final geometrical parameters are also included in Table 7. The difference in distances and angles can hardly be characterized as significant. As one would have expected, the difference between the two bond distances containing a sulfur atom has increased slightly as a result of the decrease in the corresponding u-values.

In compound II as in the parent molecule (I) $r(O1-C5) < r(O1-C2)$, but the difference appears

Table 7. Amplitudes and molecular geometry[a] for 1,3,4-oxathiazol-2-one as previously published in columns I, and in columns I′ u-values calculated from a new force field (see text) and geometry obtained when using the new set of amplitude quantities in the refinements.

Force field calculations			Electron diffraction		
	I (Ref. 1)	I′ (this work)		I (Ref. 1)	I′ (this work)[b]
u(O1 – C2)	0.0471	0.0471	1 r(O1 – C2)	1.402(3)	1.398(3)
u(O1 – C5)	0.0473	0.0475	2 r(O1 – C5)	1.356(3)	1.355(3)
u(S3 – C2)	0.0502	0.0446	3 r(S3 – C2)	1.767(2)	1.773(2)
u(S3 – N4)	0.0541	0.0468	4 r(S3 – N4)	1.690(2)	1.687(2)
u(N4 = C5)	0.0417	0.0457	5 r(N4 = C5)	1.286(2)	1.283(2)
u(O6 = C2)	0.0377	0.0398	6 r(O6 = C2)	1.192(2)	1.193(2)
u(C5 – H7)	0.0767	0.0768	7 r(C5 – H7)	1.102(19)	1.107(20)
u(S3···O1)	0.0561	0.0482			
u(N4···C2)	0.0606	0.0548	8 ∠C5O1C2	110.8(2)	110.9(2)
u(S3···C5)	0.0564	0.0509	9 ∠O1C2O6	122.6(3)	123.4(3)
u(O1···N4)	0.0532	0.0536	10 ∠C2S3N4	93.8(1)	93.7(1)
u(C2···C5)	0.0576	0.0534	11 ∠O1C5H7	114.5(31)	114.8(31)
u(O1···O6)	0.0582	0.0610			
u(S3···O6)	0.0612	0.0590	∠O1C2S3	106.3	106.2(2)
u(O1)···H7)	0.0999	0.1052	∠O1C5N4	121.1	121.2(2)
u(N4···H7)	0.0972	0.1046	∠C5N4S3	107.9	108.1(2)
u(O6···N4)	0.0638	0.0601			
u(O6···C5)	0.0615	0.0607	A[c]	5582.6(13)	5583.3(6)
u(S3···H7)	0.0940	0.0920	B	3643.8(4)	3643.3(3)
u(C2···H7)	0.0957	0.0958	C	2204.7(2)	2204.8(1)
u(O6···H7)	0.1031	0.1063			
			R(%)	9.91	9.35

[a] Distances (r) and amplitudes (u) in Å; angles (∠) in degrees; and rotational constants (A, B, C) in MHz. [b] The independent geometrical parameters are numbered. The correlation coefficients $|\rho(i,j)| > 60\%$ are $\rho(1,2) = -78$ and $\rho(10,11) = -66$. [c] The r_z representatives for the rotational constants are for column I 5582.0(16), 3643.5(7) and 2204.8(2) MHz; and for column II 5582.8(18), 3643.5(8), 2204.9(2) MHz, respectively.

Table 8. Per mille changes of ring parameters (S) and of combinations of type [O1 – C2, ∠O1C2S3, C2 – S3] *etc.* as taken counter clockwise (Fig. 4) when H of compound I is substituted by CH_3, producing II. Distances in Å angles in degrees.

	I	II	S[a]	Combination[b]
O1 – C2	1.398	1.391	5.0	
O1 – C2 – S3	106.2	106.4	1.9	9.7
C2 – S3	1.773	1.768	2.8	
C2 – S3 – N4	93.7	93.5	2.1	6.1
S3 – N4	1.687	1.685	1.2	
S3 – N4 = C5	108.2	109.2	9.2	15.1[d]
N4 = C5	1.283	1.289	4.7	
N4 = C5 – O1	121.2	119.3	15.9	29.4[c]
C5 – O1	1.355	1.367	8.8	
C5 – O1 – C2	110.9	111.8	8.1	21.9[d]
O1 – C2	1.398	1.391	5.0	

[a] Single parameter. [b] Appropriate combination. [c] Maximum change at atom C5 where CH_3 substitution occurs. [d] Changes at atoms neighbouring C5.

to be less pronounced in II [0.024(6) Å] than in I [0.044(6) Å], whereas the averages of the O–C bonds in the two compounds are rather similar [1.379(4) and 1.377(4) Å, respectively]. Inspection of the structural results for the two compounds does not suggest drastic changes in the ring geometry due to methyl substitution. The larger changes occur at C5 and its two neighbouring atoms. In fact, the ring angle (∠O1C5N4) decreases by about 2° at the site of methyl substitution and there is indicative evidence for corresponding bond elongations (*i.e.* O1–C5 and C5=N4). This is consistent with effects of methyl substitution in benzene[12,13] where a corresponding decrease in the ring angle has been related to different spatial requirements for the C–C *vs.* C–H σ-bonding electron pairs in the valence shell of the *ipso* carbon.[12] Also, the molecular structure of *p*-benzoquinone[14] in the solid state as compared to those of various methyl derivatives of *p*-benzoquinone[15] suggests the presence of similar effects of methyl substitution.

The C5–C7 bond length of 1.487(3) Å appears to be slightly shorter than the values of 1.50–1.52 Å most often found for $C(sp^3)-C(sp^2)$ bonds, as for example on the before-mentioned methyl derivatives of benzene[13] and *p*-benzoquinone.[15] However, it compares favourably with the C–C bond length of 1.484(4) Å found in $CH_3HC=N-N=CHCH_3$.[16]

The barrier to internal rotation for methyl groups attached to sp^2 type carbons in heterocyclic five-membered ring molecules has been shown to be strongly dependent on the ring type and the different positions in the rings.[17] For II the rotational barrier of 5.98 kJ mol^{-1} (1.43 kcal mol^{-1}) is, for example, larger than that of 2-methylfuran, $CH_3-C=CH-CH=CH-O$, reported to be 1.19 kcal mol^{-1}.[18]

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