THE ROTATIONAL AND VIBRATIONAL SPECTRA, STRUCTURE AND DIPOLE MOMENT OF 1,3-DIOXOLE-2-THIONE

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ABSTRACT

Rotational and centrifugal distortion constants are determined for the ground state and several excited states of the lowest vibrational mode of 1,3-dioxole-2-thione, the "envelope" ring-bending mode. The structure of the molecule is planar. The A-constant is 1% larger than that of 1,3-dioxole-2-one (vinylene carbonate), which indicates small changes in ring-geometry on substituting C=S for C=O. The dipole moment of 1,3-dioxole-2-thione deduced from Stark-effect measurements is $(1.60 \pm 0.02) \times 10^{-29}$ Cm (4.81 ± 0.06 D). IR and Raman spectra lead to a complete analysis of the normal modes of vibration, based partially on a normal coordinate calculation.

INTRODUCTION

Heterocyclic five-membered ring structures have been much studied in recent years. One class of such compounds which merits closer investigation is the derivatives of 1,3-dioxole, where detailed studies have been confined to 1,3-dioxole-2-one (vinylene carbonate) (1) [1-6]. While this substance has a planar equilibrium geometry, studies of the Zeeman effect [6] indicate no aromatic character. We report here the first detailed spectroscopic studies of the corresponding thione, in which C=O is replaced by C=S (2).



EXPERIMENTAL

The sample of 1,3-dioxole-2-thione was prepared by the action of P_4S_{10} on vinylene carbonate [7]. The product, purified by vacuum distillation, consisted of long, white, needle-like crystals with a garlic-like odour (m.p. 45°C; C = 35.45%, H = 2.1%). The pure rotation spectrum was measured using a

conventional 100-kHz Stark-modulated microwave spectrometer, with a 3-m X-band copper cell. Free running klystrons and oscilloscope presentation were used throughout; all measurements were carried out with the cell at room temperature. Absorption frequencies, measured using a Hewlett-Packard 5341A frequency counter, are believed to be accurate to ± 0.1 MHz. IR spectra were recorded with a Perkin-Elmer 225 spectrometer using cells with CsI optics. The spectrometer calibration was checked using the absorption bands of polystyrene and band positions are believed to be accurate to ± 1 cm⁻¹ The Raman spectra were kindly recorded by Dr. R. Hester (University of York).

ROTATIONAL SPECTRUM

Assignment of spectroscopic constants

1,3-Dioxole-2-thione is a near-prolate rotor ($\kappa = -0.88$) with a predicted rotational spectrum comprising many strong μ_A *R*-branch transitions between 13 and 40 GHz. The observed spectral pattern was readily assigned from predictions based on a molecular structure deduced from the known geometry of 1,3-dioxole-2-one [4] and reasonable C=S distances. Only *a*-type transitions have been observed, in accord with a planar structure with C_{2v} symmetry about the *A*-axis, as discussed below.

As expected for a molecule possessing at least one vibrational mode of low frequency, each transition consisted of several lines due to molecules in the ground and excited vibrational states. In assigning lines to the ground state and to particular excited states, it was necessary to remember that, on any reasonable molecular model, the vibrational mode concerned is likely to be of symmetry species B, and that the nuclear statistical-weight factors in the rotational transition intensities, which arise from the equivalence of the two H nuclei with respect to the A-axis, will strongly affect the relative intensities of lines due to a common rotational transition in different vibrational states. This situation, which is similar to that already described for vinylene carbonate [2], was confirmed by the observations and allowed ready recognition of the lines due to the various states. For transitions with K_{-1} odd, the ground-state lines are favoured by the statistical weights and are easily the strongest lines of the group; for K_{-1} even, the V=1 state has a statistical weight of 3 relative to the ground state and two lines of comparable intensity were observed, of which the stronger fitted the assignments from the K_{-1} odd transitions of the ground state. Ground-state assignments could accordingly be made for a large number of transitions. Values of the rotational and centrifugal distortion constants for this state were obtained from a least-squares fit [8] of 67 transition frequencies. The distortion constant τ_{aabb} , which is expected to be very small (ca. 0.001 MHz), could not be evaluated and was set to zero. Table 1 lists the values of the constants. The frequencies computed from the constants agreed with the observed frequencies in most cases to within less than 0.1 MHz and in all cases to within 0.25 MHz. A list of

	Ground state	$V_{12} = 1$	<i>V</i> ₁₂ = 2	<i>V</i> ₁₂ = 3
A	9453.22(15)	9388.23(2.00)	9324.18(2.00)	9624.96(3.60)
В	2313.040(5)	2315.27(2)	2317.52(2)	2319.74(4)
С	1857.950(3)	1860.82(2)	1863.72(2)	1866.59(4)
$\tau_{anaa} \times 10^3$	-33.6(17.0)			
$\tau_{bbbb} \times 10^3$	-0.78(11)			
$ au_{abab} imes 10^3$	-1.98(4.0)			
I _A	53.4607(9)	53.831(10)	54.201(11)	54.547(21)
I_B	218,4899(5)	218.280(2)	218.068(2)	217.859(4)
Ī _C	272.0072(4)	271.588(2)	271.165(3)	270.748(6)
$\Delta(I_C - I_A - I_B)$	0.0566(10)	-0.523(11)	-1.103(12)	-1.658(22)

Spectroscopic constants (MHz), and moments of inertia and inertial defects $(a.m.u. A^2)^a$

^aFigures in parentheses indicate two standard deviations in the final figures quoted; conversion factor 505376 a.m.u. A² MHz; τ_{aabb} is assumed to be zero.

observed frequencies, with assigments, is available from B.L.L.D. as Sup. Pub. No: Sup. 26137 (3 pages).

Assignment of the rotational transitions of molecules in excited vibrational states shows that the vibrational states concerned are the V = 1, 2 and 3 levels of the same mode of symmetry species B. This followed from the variations, with V and with the parity of K_{-1} , of the statistical-weight factors adopted in identifying the intensity patterns of satellites. The rotational constants for these states are also included in Table 1. The quality of fitting for observed and calculated frequencies (list of frequencies available from B.L.L.D. for 51 assigned transitions) was comparable with that for the ground-state fitting. The assignments to V = 1, 2 and 3 states of the same mode are confirmed by the uniformity of the changes in rotational constants with increasing value of V.

Relative intensity measurements were made between the V = 0, 1, and 2 members of a given rotational transition in a number of cases, using the method of Esbitt and Wilson [9], statistical weight factors being applied, as indicated above, for a *B*-species vibration of a molecule with C_{2v} symmetry. The energy levels of the V = 1, 2 states, relative to the ground state, were found to be: V = 1, 240 ± 40 cm⁻¹; V = 2, 480 ± 60 cm⁻¹. These numbers again agree with the assignment to excited levels of a single, essentially harmonic, vibration, with the fundamental near 240 cm⁻¹.

The inertial defect, $\Delta(I_C - I_A - I_B)$ (Table 1), for the ground state has a small positive value comparable with that found for vinylene carbonate. This leaves no doubt that the equilibrium geometry is planar. The inertial defect (Table 1) moves smoothly to increasingly negative values with increasing vibrational excitation. These negative contributions to Δ show that the vibration concerned is an out-of-plane mode. The vibrational assignment (below) confirms that this mode is the "envelope" ring-bending vibration of symmetry species B_1 . The evidence shows clearly that, as in vinylene carbonate, this vibration is essentially harmonic, with a single potential minimum at the planar conformation.

Individual structure parameters cannot, of course, be calculated from the present data. It may be noted, however, that I_A for 1,3-dioxole-2-thione is some 1% less than I_A found in vinylene carbonate [2], whereas these moments of inertia should be the same for identical ring structures. The ring in the thione is thus measurably "slimmer" than in the corresponding ketone. In a model, this is perhaps best attributed to a change in the ring angles: if the ring bond-lengths are kept the same as those in vinylene carbonate, an increase of about 1° in the ring angle COC, with reductions of some 1° and 0.5°, respectively, in the ring angles OCO and OCC, leads to the observed change in I_A . With such models, the observed constants can be fitted with a C=S distance of about 160 pm. Different considerations would of course apply if the lengths of the ring bonds were altered on going from C=O to C=S, and if, as is possible, certain ring bonds become longer in this process, a shorter C=S distance would be indicated.

We have made provisional assignments of some twelve rotational transitions of the sulphur-34 form of 1,3-dioxole-2-thione, in accordance with constants in which A retains the same value and B and C agree with the approximate model discussed above.

Dipole moment

The electric dipole moment was determined from the Stark effects in the microwave spectrum. The spectrometer was calibrated using the $J \ 2 \leftarrow 1$ transition of OCS, the moment of which was taken [10] as 0.71521 D. The Stark shifts of a total of 17 line-components were measured, all of which were found to follow the expected second-order behavioural pattern. The results including our final value for the dipole moment ($\mu = \mu_a = 4.81 \pm 0.06$ D or 1.60×10^{-29} Cm), are shown in Table 2. The observed value is strikingly arge but is comparable in magnitude to the 4.57 D (1.52×10^{-29} Cm) measured for vinylene carbonate [1, 2].

As with vinylene carbonate [2] the dipole moment is the same, within the measurement errors, for both the first excited state of the "envelope" ing-bending mode and for the ground state.

VIBRATIONAL SPECTRUM

For this planar molecule of C_{2v} symmetry, 18 fundamental vibrations are listributed as follows amongst the four symmetry species: A_1 (7 modes), A_2 (2 modes), B_1 (3 modes) and B_2 (6 modes). All vibrations are expected to be Raman active, but the A_2 modes are not active in the IR.

Spectra of 1,3-dioxole-2-thione were obtained for the solid phase and for solutions in CCl_4 and CS_2 , and the vapour pressure was sufficient at ambient

Transition (ground state unless otherwise indicated)	М	$\Delta \nu / E^2$ (MHz V ⁻² cm ² × 10 ⁶)	μ(D)
$3_{13} \rightarrow 4_{14}$	1	7.70	4.80
	2	56.61 ·	4.83
$3_{1,2} \rightarrow 4_{1,3}$	0	- 7.50	4.81
- 12 - 12	1	-15.32	4.82
	2	38.54	4.81
$5_{1.5} \rightarrow 6_{1.6}$	0	- 3.01	4.76
	1	-1.83	4.75
	2	1.70	4.81
	3	7.65	4.81
	4	15.92	4.80
	5	26.68	4.81
$5_{0.5} \rightarrow 6_{0.6}$	3	1.67	4.82
- -	4	5.87	4.81
	5	11.21	4.80
$5_{0,5} \rightarrow 6_{0,6}$	2	- 1.35	4.81
$(V_{12} = 1 \text{ state})$	3	1,58	4.81
· ••	4	5.85	4.81

Stark coefficients and dipole moment. Mean dipole moment $\mu = \mu_{\alpha} = 4.81 \pm 0.06$ D

temperatures for some of the strongest absorptions to be recorded for the gaseous phase. These were seen to have characteristic contours corresponding to A, B and C types (Table 3).

Preliminary assignments of modes were made in the usual way, but it was judged appropriate to obtain the most satisfactory overall assignments, and also force-field information, by use of a least-squares refinement program recently described by Christen [11]. The input of this program, in addition to the approximate geometric model derived above, consisted of vibrational frequencies, inertial defects, and force constants taken initially from tables of standard values for specified motions of particular groupings. For the best overall fit, a number of interaction constants were given values, although many remained set at zero. Table 3 shows the allocation of observed frequencies to modes and their combinations. Table 4 lists the values of the force constants given by the final iterations, while Table 5 summarizes the final overall fitting of the 18 mode frequencies and the inertial defects. Table 5 also includes the "trivial descriptions" of modes, but our procedure makes it very clear that many vibrations are not localized in groups of atoms. The right-hand column of Table 5 shows the contributions of those force constants which mainly determine particular mode frequencies; the potential energy distribution is reasonable on general grounds, but, while for most modes

IR and Raman spectra of 1,3-dioxole-2-thione^a

Vapour		IR		Raman	Interpretations	
		Band type	Solution ^b or solid	(solid)		
3225 R)						
3215 ctr 3205 P	vw	В	3230 m		<i>v</i> ₁₃	
3142 <i>R</i> 3138 <i>Q</i>	w	A	3160 s		ν_1	
3131 P '			2624 w		$2\nu_{a}$	
			2418* w		$\nu_{14} + \nu_{16}$	
			2372 m		$v_{1} + v_{2}$	
			2181 m		$v_3 + v_6$	
			2006 w		$v_{4} + v_{6}$	
			1955 mw		$2\nu_6 + \nu_{12}$	
			1867 m		$\nu_3 + \nu_7$	
			1838 vw		$2v_7 + v_{11}$	
			1770* w		$v_6 + v_7 + v_{18}$	
			1728 mw		$2\nu_6$	
			1634* m	1628 vw	ν_2	
				1613 w	$\nu_7 + \nu_{15}$	
			—	1604 m	?	
			1380 mw		ν_{14}	
1040 0			—	1352 w	$ u_8 $	
1340 R 1335 Q 1327 P	vs	A	1313 vs	1324 w	ν_3	
1154 0.			1275 m	1288 m	ν_{10}	
$\left.\begin{array}{c}1154 \\ 1154 \\ 1148 \\ 1141 \\ P\end{array}\right\}$	ms	A	1142 s	1148 m	v ₄	
1004 0			1110 w		$2\nu_{\gamma}$	
$ \begin{array}{c} 1094 & R \\ 1089 & Q \\ 1080 & P \end{array} $	m	Α	1070 s		ν _s	
1054 R 1048 ctr	m	В	1062 s	1056 ms	<i>v</i> ₁₅	
1042 P			1032 m	1034 w	V	
			905 w	1001 11	$\nu_{7} + \nu_{10}$	
			896 w		$v_{12} + v_{17}$	
862 R V					12 11	
857 Q 852 P	m	Α	864 s	888 s	ν ₆	
728 <i>B</i> 1						
721 Q 711 P	m	С	725 ms		ν ₁₁	

TABLE 3 (cont.)

Vapour	IR		Raman	Interpretations	
	Band type	Solution ^b or solid	(solid)		
		669 m	678 w	ν ₁₇	
		555 m	556 s	ν _η	
		—	542 w	vg	
		352* m	352 w	V 18	
		221* m	_	ν_{12}	
		-	80		
		_	56		
		—	40		

^aFrequencies in cm⁻¹; s = strong, m = medium, w = weak, vw = very weak.

^bValues refer to solutions in CS_2 , except those values with an asterisk, which are for the solid.

a single force constant makes a contribution of more than 50% to the potential energy, less than half the vibrations are dominated by just one force constant.

The molecular dipole moment lies along the symmetry axis, and consequently many vibrations of symmetry class A would be expected to show quite strong absorptions. This is clearly seen for the mode which is largely associated with the stretching motion of the C=S bond at 1313 cm⁻¹, and for the symmetric stretching vibration of the CH bonds at 3160 cm⁻¹. Other strong A_1 vibrations include the skeletal C=C stretching mode at 1634 cm⁻¹, the symmetric C—H deformation mode at 1142 cm⁻¹, and three skeletal deformation movements involving stretching of the C—O bands and bending of the C—O—C and O—C—S angles at 1070, 864 and 555 cm⁻¹, respectively.

The two A_2 vibrations arising from the twisting mode of the C—H bonds and from a ring puckering are assigned to absorptions observed in the Raman spectrum at 1352 cm⁻¹ and 542 cm⁻¹.

One of the absorptions obtained in the vapour phase at 721 cm⁻¹ showed a C-type band contour with a strong central Q branch, and consequently we assign this band to an out-of-plane C=S mode of the B_1 class. Of the two other B_1 modes, the C—H wagging vibration is assigned to an absorption at 1275 cm⁻¹, higher than the corresponding mode in vinylene carbonate [5], whilst the remaining out-of-plane ring mode must correspond to the lowest frequency vibration at 221 cm⁻¹.

Some of the vibrations with B_2 symmetry were assigned on the evidence of their *B*-type contours in the spectrum of the vapour, e.g. the antisymmetric C-H stretch at 3215 cm⁻¹ and the antisymmetric C-O-C stretch at 1048 cm⁻¹.

It is worth noting that, while the vibrational assignment presented here is satisfactory and internally consistent, it is not impossible that reassignment of certain modes will be indicated when more data are available. For example,

Observed and calculated vibrational frequencies (cm^{-1}) and potential-energy distribution in normal modes of 1,3-dioxole-2-thione, with observed and calculated inertial defects (a.m.u. λ^2)

Mode	Frequen	су су	Approx. description	Potential energy distribution ^a	
	Obs.	Calc.			
Species A	·				
ν,	3160	3160	C—H sym. str.	C—H str. (100)	
ν_2	1634	1640	C=C str.	C=C str. (35); C=C-H bend (29)	
v_3	1313	1311.9	C=S str.	C=S str. (70); O(1)-C(2) str. (19)	
ν_4	1142	1136.9	C=C—H sym, i.p. bend	C=C—H bend (37); C=C str. (28)	
ν_{5}	1070	1067.4	Skel. str.	$ \begin{array}{l} \{ O(1) - C(2) \text{ str. } (31); O(1) - C(5) \text{ str. } (27) \\ O(1) - C(2) \text{ str. } (O(3) - C(2) \text{ str. } (21) \end{array} $	
ν ₆	864	871.4	Skel. str.	$\begin{cases} O(1) - C(5) \text{ str. } (51); O(1) - C(2) \text{ str. } (24) \\ O(1) - C(2) \text{ str. } (O(3) - C(2) \text{ str. } (16) \end{cases}$	
ν ₇	555	548.1	Skel. i.p. bend	C—O—C bend (45); C=S str. (30)	
Species A					
V.	1352	1351.7	C—H twist	C—H 0.0.p. bend (80); ring twist mode (20)	
ν_{0}^{*}	542	540.5	Ring bend, twist mode	Ring twist mode (79); C-H o.o.p. bend(20)	
y Species B	,				
abectes p	1 1975	1974 0	C-H war	(C-Hoon bend (80); C-Hoon bend/	
- 10	1210	1214.5		$C-H \circ \circ p$ bend (18)	
ν	725	724.7	C=S wag	C=S o.o.p. bend (88); ring envelope mode (11)	
ν_{12}	221	236.1	Ring-bend, envelope mode	ring envelope mode(87); C=S o.o.p. bend (11)	
Encoice B	•				
Species B	2 2 2 2 0	2220.4	C-Hanticum str	C-H str (97)	
^ν 13	1380	1382 1	C=H antisym, str. C=C=H antisym i n hand	C = C - H hered (102): $O(1) - C(5) = C(4)$	
- 14	1000	1002.1	0°0 II antaym. 1.p. benu	bend/G(4)=C(5)-H bend (-19)	
ν_{15}	1062	1071.1	Skel. str.	C-O-C bend(30); $O(1)-C(2)$ str./ $O(3)-$	
				C(2) str. (-35)	
	1			0(1)-C(5) str. (36); $0(1)-C(2)$ str.(10)	
v16	1032	1020	Skel. str.	C-O-C bend (13); OC=C bend (19)	
v 17	669	675.3	Skel. bend	O(1)-C(2) str. (80); $O(1)-C(5)$ str. (12) O-C=C bend (35); $O(1)-C(2)$ str./ $O(3)-C(2)$ str./ $O(3)$ -	
V	352	339 1	C=Sin hend	0 - C = S bend (47); 0(1)-C(2) str. (40)	
- 18	000	005.4	oro np. beng	C-O-C Bend(11)	
Inertial defects	Obs.	Calc.			
Δ_{0}	0.0566	-0.077			
<u>د</u>	-0.523	-0.509			
Δ_2	-1.103	-0.942			
د.	-1.658	-1.374			

^aFigures in parentheses are % contributions of the stated force constants (see Table 5) (major contributions only).

the species A_1 skeletal-stretch modes depend predominantly on the force constants for O(1)-C(2) and O(1)-C(5) stretching. We have chosen an interpretation in which O(1)-C(2) has a somewhat higher stretching constant than O(1)-C(5), which is consistent with the expectation that O(1)-C(2) will be a shorter band than O(1)-C(5), as in vinylene carbonate. The distances in the present molecule are, however, unknown and adjustments to the vibrational assignment may be necessary when more detailed geometric information is available.

Description	Force constant ^a	Description	Force constant ^a
C=C str.	6.073	C-H o.o.p. bend	0.778
C-H str.	5.546	C=S o.o.p. bend	0.797
O(1)-C(2) str. O(1)-C(5) str.	4,421 4,050	Interaction constants C(4)—H o.o.pbend/C(5)—H	0.180
C=S str. C=C-H i.p. bend	8.681 1.112	o.o.pbend O(1)C(2) str./O(3)C(2)	2.732
O-C=S i.p. bend	1.097	str.	
C—O—C i.p. bend O—C=C i.p. bend	2.511 1.433	O(1)-C(5)=C(4) bend/C(4) =C(5)-H bend	0.630
Ring-bending (twist mode)	0.535	C(4)-H str./C(5)-H str.	-0.137
Ring-bending (envelope mode)	0.115	C(4)=C(5)—H bend/C(5)= C(4)—H bend	0.137
		C=S str./O(1)-C(2) str.	2.739
		O(1)-C(2) str./C-O(1)-C bend	0.305

Force-constants from least-squares refinement program for vibrational assignments in 1,3-dioxole-2-thione

^a Units: stretch and stretch/stretch interactions, mdyne A⁻¹; bend and bend/bend inter actions, mdyne A rad⁻²; stretch/bend interactions, mydne rad⁻¹.

The vibrational assignment corresponds well with that for vinylene carbonate [5]. An interesting point of similarity between the two substances is seen in the frequencies for the C=O and C=S stretching modes. In vinylene carbonate the C=O stretching frequency is high, at 1864 cm⁻¹, and is accompanied by a somewhat short C=O internuclear distance at 119 pm. In the thione the C=S stretching frequency, v_3 , at 1313 cm⁻¹, is high for such a mode, which usually appears in the range 1020-1250 cm⁻¹, although this mode is susceptible to coupling effects [12]. Here it is associated with a bond length which is unlikely to exceed the "normal" value of ca. 161 pm found in thioaldehydes [13]. An interesting comparison can be made with the corresponding modes and distances in the ring systems 4-pyrone and 4-thiapyrones. In 4-pyrone, the C=O stretching frequency is ca. 1670 cm^{-1} [12] and the C=O distance is 123 pm [14], while in pyr-4-thione and thiapyr-4-thione the C=S stretching mode is assigned near 1100 cm^{-1} [15, 16]. This value is 15% lower than the corresponding value in 1,3-dioxole-2-thione, and is accompanied, for example in this try-4-thione [17], by a large C=S distance of 167 pm.

As a check on our procedure, we also applied Christen's least-squares refinement program to the data on vinylene carbonate given by Durig et al. [5], and obtained general agreement with the assignments made by these workers. However, it is possible that small adjustments in the allocation of modes which depend on the force constants connected with the CH groups would improve the overall consistency.

Thermodynamic properties

On the basis of the rotational and vibrational assignments for 1,3-dioxole-2-thione, we have calculated, by standard procedures, the gas-phase thermodynamic functions at three temperatures, and these are listed in Table 6. These are the first published estimates of these properties.

DISCUSSION

Some aspects of the properties of 1,3-dioxole-2-thione and of vinylene carbonate may usefully be compared with corresponding very detailed data which are now available [18, 19] for cyclopent-3-enone. The planarity of the dioxole structures is itself not surprising, since the heavy-atom structure of the ring is also planar in cyclopent-3-enone, where both ring oxygens have been replaced by methylene groups. The envelope ring-puckering mode of cyclopent-3-enone, however [19], has the very low frequency of 83 cm⁻¹, and the much higher frequencies observed for this mode in the dioxole derivatives, even when C=O is replaced by C=S, point to a considerably more rigidly planar ring in the dioxole structures. The C=O distance in cyclopent-3-enone [18] is 121 pm, 2 pm greater than that in vinylene carbonate, while the dipole moment of cyclopent-3-enone, 2.79 D [18] increases dramatically to 4.57 D when the ring methylene groups are substituted by oxygen. The moment of 1,3-dioxole-2-thione is even larger. One of the most striking properties of this substance and of vinylene carbonate is their high polarity,

TABLE 6

Thermodynamic functions calculated for 1,3-dioxole-2-thione from spectral data^a

Temp. (K)	Contribution	$(H-E_{o})/T$	$-(G-E_o)/T$	S	Cp
298.16	Translation	4.9680	34.8085	39.7765	4.9680
	Rotation	2,9808	22.1166	25.0974	2.9808
	Vibration	3.4520	1.7034	5.1554	9.3994
	Total	11.40	58.63	70.03	17.35
400.00	Translation	4.9680	36.2683	41.2363	4.9680
	Rotation	2.9808	22.9924	25.9732	2.9808
	Vibration	5.5629	2.9954	8.5583	13.8097
	Total	13.51	62.26	75.77	21.76
800.00	Translation	4.9680	39.7118	44.6798	4.9680
	Rotation	2.9808	25.0585	28.0393	2.9808
	Vibration	12.9469	9.2691	25.2589	24.9361
	Total	20.90	74.04	97.98	32.88

^aH = enthalpy, E = internal energy, G = Gibbs free energy, S = entropy and C_p = heat capacity at constant pressure; subscript zero indicates zero-point value (cal mol⁻¹ K⁻¹).

from which it is necessary to conclude that the rings acquire appreciable positive charge, balanced by negative charge on the carbonyl oxygen or the sulphur atom, respectively. The electron-drifts concerned appear to lead to C=O and C=S lengths which are less than those in "normal" ketones and thicketones, and to confer extra rigidity on the planar ring-structure.

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