Structure and Dipole Moment of 1,6-Dioxa-6aλ⁴-thiapentalene from Microwave Spectra

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Dedicated to Professor K. A. Jensen on his 70th birthday

The microwave spectra of 1,6-dioxa-6aλ⁴-thiapentalene and its 3,4-D₂ derivative have been analysed. No evidence of valence tautomerism has been found. All observations so far indicate a planar molecule with C_{2v} symmetry. The electric dipole moment has been found to be 3.07 ± 0.04 D.

Compounds of the type illustrated in Fig. 1 where X, Y, Z are O, S, Se etc. have been quite intensively studied in recent years, with the aim of establishing the character of the so-called "electron rich three-center bond" $X-Y-Z$.[1] Numerous X-ray crystallographic studies in the $X=Y=Z=S$ case (trithiapentalene) have revealed curious properties of this bond. Thus it has been found that even in the case of symmetrical substitution different $S-S$-bond lengths may result (cf. Ref. 2 and further references cited there). Such findings led to speculations as to whether the molecule exhibited valence tautomerism as depicted in Fig. 2, or, equivalently, whether the molecule has a double minimum potential in its electronic ground state. Molecular orbital calculations could not rule out such ideas.[1]
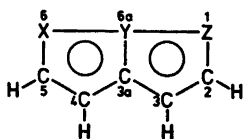

Fig. 1. Homologues of 1,6,6aλ⁴-trithiapentalene considered as systems with a specific structure.

ESCA measurements in the vapour phase seemed to indicate a C_{2v}-symmetric structure,[3] and this was very strongly supported by a structure determination by electron diffraction (ED).[4] Large amplitudes of vibration of the SS-bonds were taken as evidence of the "bell-clapper" effect suggested in Ref. 1. This effect in fact means that the central (6a) sulfur atom is situated either in a flat single minimum, or in a double minimum with a rather low central hump. ED can hardly discriminate between these possibilities since an average over the Boltzmann distribution is observed. The controversy has therefore not been entirely settled.

Microwave spectroscopy should be particularly well suited to enlighten such matters for several reasons (see below). Attempts to study trithiapentalene failed however, because the vapour pressure of this substance is too low at room temperature. Corkill, Cox and Ewart made an attempt to study the molecule in a heatable spectrometer, but the substance decomposed.[5]

1,6-Dioxa-6aλ⁴-thiapentalene ($X=Z=O$, $Y=S$ in Fig. 1) does have sufficient vapour pressure and in fact turned out to have a very intense microwave spectrum. Assuming a rigid, planar model with C_{2v} symmetry, approximate
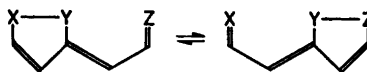

Fig. 2. Homologues of 1,6,6aλ⁴-trithiapentalene considered as mixtures of valence tautomers.

moments of inertia and the rotational spectrum could be predicted with sufficient accuracy to allow an assignment of the spectrum as we shall see below.

EXPERIMENTAL

Microwave spectra were obtained on a Hewlett-Packard MRR-spectrometer.

The parent molecule and the deuterated sample were prepared according to the description by Reid and Webster.[6] The vapour pressure was estimated on a Pirani manometer to be ca. 0.1 mmHg at 25 °C.

Measurements of microwave frequencies in the ground state of both isotopic species were made at −10 °C at a pressure in the range 0.01−0.03 mmHg. The excited states at room temperature are in the same range of pressure. The accuracy of the frequencies is ca. 0.03 MHz. (cf. Tables 1−7).

ASSIGNMENTS AND INTERPRETATIONS

Due to their extreme sensitivity to the model we at first had some difficulty in assigning the

Table 1. Rotational transitions of dioxathiapentalene in the vibrational ground state.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	Frequency/MHz ν_{obs}	$\nu_{obs} - \nu_{calc}$ [a]
2	2	0	3	3	1	22588.530	0.006
2	2	1	3	3	0	22653.840	−0.005
3	2	2	4	3	1	25669.550	0.011
3	2	1	4	3	2	25339.710	−0.048
4	3	1	5	4	2	33966.330	0.017
6	0	6	7	1	7	18359.080	0.009
7	1	7	8	0	8	20258.530	−0.015
10	0	10	11	1	11	27665.910	0.021
11	0	11	12	1	12	30055.560	0.002
11	1	11	12	0	12	30030.550	−0.014
12	0	12	13	1	13	32451.670	0.023
12	1	12	13	0	13	32439.300	−0.010
12	1	11	13	2	12	35093.660	0.013
12	2	11	13	1	12	34677.660	−0.002
13	5	9	13	6	8	29793.260	−0.013
13	6	8	13	7	7	35590.510	0.002
13	0	13	14	1	14	34851.070	−0.007
13	1	13	14	0	14	34845.040	−0.013
14	5	9	14	6	8	28415.350	0.005
14	6	8	14	7	7	35275.330	0.001
15	5	11	15	6	10	29578.710	−0.018
15	6	10	15	7	9	35159.230	0.007
16	6	10	16	7	9	34399.030	0.002
17	3	15	17	4	14	30405.940	−0.005
17	4	14	17	5	13	28224.600	−0.001
17	5	13	17	6	12	29826.740	0.004
17	6	12	17	7	11	34672.280	0.002
18	2	16	18	3	15	31253.390	0.015
18	4	15	18	5	14	29718.870	−0.010
18	6	12	18	7	11	32712.560	0.010
18	6	13	18	7	12	34469.180	0.005
19	6	14	19	7	13	34346.070	−0.015
20	4	17	20	5	16	33424.440	0.001
20	6	14	20	7	13	29812.910	0.030
20	6	15	20	7	14	34352.340	0.001
24	5	19	24	6	18	24585.530	0.003
24	7	17	24	8	16	33372.530	−0.025
27	6	21	27	7	20	25645.750	0.021
29	6	23	29	7	22	31468.850	−0.015
29	7	22	29	8	21	26375.550	0.005

[a] Rms deviation: 0.0160.

Table 2. Rotational transitions of dioxathiapentalene in the $v_a = 1$ vibrational state.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	Frequency/MHz ν_{obs}	$\nu_{obs} - \nu_{calc}$ [a]
7	0	7	8	1	8	20624.620	− 0.001
8	0	8	9	1	9	22944.225	− 0.035
8	1	8	9	0	9	22755.535	0.016
8	2	7	9	1	8	23585.450	0.019
12	3	10	12	4	9	21858.705	− 0.061
12	4	9	12	5	8	24617.095	0.040
18	5	13	18	6	12	22813.210	0.016
19	4	15	19	5	14	18807.555	0.024
19	5	14	19	6	13	21403.850	0.009
20	5	15	20	6	14	20452.730	− 0.007
21	4	17	21	5	16	23692.590	0.011
21	5	16	21	6	15	20182.725	− 0.016
24	6	18	24	7	17	23488.925	0.011
25	6	19	25	7	18	23249.810	− 0.030

[a] Rms deviation: 0.0294.

Table 3. Rotational transitions of dioxathiapentalene in the $v_s = 1$ vibrational state.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	Frequency/MHz ν_{obs}	$\nu_{obs} - \nu_{calc}$ [a]
2	2	0	3	3	1	22576.600	− 0.069
3	2	2	4	3	1	25654.565	0.031
8	0	8	9	1	9	22938.680	0.010
8	1	8	9	0	9	22746.655	− 0.089
8	2	7	9	1	8	23559.030	0.045
9	0	9	10	1	10	25294.735	0.025
9	1	9	10	0	10	25195.065	0.014
13	3	11	13	4	10	23108.870	− 0.026
19	4	15	19	5	14	18800.090	0.008
19	5	14	19	6	13	21533.170	0.008
20	5	15	20	6	14	20555.230	0.002
21	5	16	21	6	15	20248.940	0.017
22	5	17	22	6	16	20765.615	− 0.001
24	6	18	24	7	17	23609.140	− 0.002
25	6	19	25	7	18	23322.055	0.020

[a] Rms deviation: 0.0390.

Table 4. Rotational transitions of dioxathiapentalene in the $v_a' = 1$ vibrational state.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	Frequency/MHz ν_{obs}	$\nu_{obs} - \nu_{calc}$ [a]
2	2	1	3	3	0	22640.700	0.030
7	0	7	8	1	8	20518.810	0.005
7	1	7	8	0	8	20153.540	0.016
8	1	8	9	0	9	22627.280	− 0.016
8	2	7	9	1	8	23421.605	− 0.014
12	3	10	12	4	9	21940.375	− 0.017
18	5	13	18	6	12	23090.920	− 0.012
19	4	15	19	5	14	18785.850	− 0.077
19	5	14	19	6	13	21652.355	0.024
21	4	17	21	5	16	23552.215	0.045
21	5	16	21	6	15	20307.280	− 0.002
25	6	19	25	7	18	23386.020	0.006

[a] Rms deviation: 0.0345.

Table 5. Rotational transitions of dioxathiapentalene in the $v_a = 2$ vibrational state.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	Frequency/MHz ν_{obs}	$\nu_{obs} - \nu_{calc}$ [a]
8	1	7	9	2	8	26967.560	0.081
9	2	8	10	1	9	26644.410	0.007
10	0	10	11	1	11	27696.900	0.015
11	5	7	11	6	6	29889.150	−0.009
11	2	10	12	1	11	32140.690	0.004
12	0	12	13	1	13	32490.170	−0.018
13	5	9	13	6	8	29556.010	−0.028
14	0	14	15	1	15	37298.110	−0.040
14	1	14	15	0	15	37295.260	−0.012
15	5	11	15	6	10	29343.920	0.033
18	6	12	18	7	11	32444.500	−0.012
20	6	14	20	7	13	29561.770	0.004

[a] Rms deviation: 0.0353.

Table 6. Rotational transitions of dioxathiapentalene in the $v_s = 2$ vibrational state.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	Frequency/MHz ν_{obs}	$\nu_{obs} - \nu_{calc}$ [a]
11	2	10	12	1	11	32111.540	−0.003
12	0	12	13	1	13	32467.730	0.003
36	9	27	36	10	26	32413.230	−0.029
38	9	29	38	10	28	33209.650	0.002
38	10	28	38	11	27	38352.370	−0.012
39	10	29	39	11	28	36381.480	0.034
42	10	32	42	11	31	36302.550	0.003

[a] Rms deviation: 0.0232.

Table 7. Rotational transitions of 3,4-D_2-dioxathiapentalene in the vibrational ground state.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	Frequency/MHz ν_{obs}	$\nu_{obs} - \nu_{calc}$ [a]
7	0	7	8	1	8	19791.140	−0.032
7	1	7	8	0	8	19590.970	0.074
8	0	8	9	1	9	22053.825	0.009
8	1	8	9	0	9	21955.470	−0.011
9	0	9	10	1	10	24342.360	−0.018
9	1	9	10	0	10	24295.280	−0.014
18	5	13	18	6	12	18240.115	−0.044
20	4	16	20	5	15	23107.780	−0.066
20	5	15	20	6	14	18046.380	0.004
21	5	16	21	6	15	19288.340	−0.010
21	6	15	21	7	14	21692.090	−0.001
22	5	17	22	6	16	21438.950	0.018
23	5	18	23	6	17	24355.080	0.016
23	6	17	23	7	16	20429.460	0.040
24	6	18	24	7	17	21152.415	0.052
25	6	19	25	7	18	22876.465	−0.046
26	6	20	26	7	19	25516.710	0.031

[a] Rms deviation: 0.0392.

Table 8. Term values (cm^{-1}) calculated from Boltzmann factors for the $v_a = 1$, $v_s = 1$ and $v_a' = 1$ states.

Transition J''	K_{-1}''	K_{+1}''	J'	K_{-1}'	K_{+1}'	ν_a	ν_s	ν_a'
15	2	13	15	3	12	234	278	314
19	5	14	19	6	13	170	168	248
21	5	16	21	6	15	238	298	252
22	5	17	22	6	16	234	268	262
23	5	18	23	6	17	205	241	246
25	6	19	25	7	18	189	239	281
26	6	20	26	7	19	187	237	297
27	6	21	27	7	22	227	247	316
Mean values						211	247	277

spectra. However, once a suitable model was found, the turning point of the $J_{1,J-1} - J_{2,J-2}$ Q-branch was easily located. Low-J R lines were found by assuming zero inertial defect I.D. (defined in Table 9). Spectra of five excited vibrational states were also assigned for the parent molecule. The spinweights 10:6 were very helpful in the assignments. Two of the three most prominent excited states were found to have spinweights opposite to the ground state, while the third had the same spinweights. They are referred to as the $v_a = 1$, $v_a' = 1$ and $v_s = 1$ states respectively (see below), the remaining are the $v_a = 2$ and $v_s = 2$ states, both having the same spinweights as the ground state. We have tried in vain to assign the $v_a' = 2$ state, the number of lines with comparable intensity being very large. The index "a" means that the state concerned has an antisymmetric vibrational wave function, and "s" a symmetric with respect to the twofold axis of the C_{2v} point group. The term values of the

$v = 1$ states have been determined from relative intensity measurements, *cf.* Table 8. These values have been corroborated by the far-IR and Raman spectra (see below).

The spectrum of the deuterated molecule was sufficiently well predicted by the same model to be easily assigned. Several attempts have been made to observe the spectrum of the ^{34}S-substituted molecule in natural abundance (4 %). But since this spectrum is of an intensity comparable to that of the $v_a' = 2$ state, we have not been successful so far.

Tables 9 and 10 contain the rotational and centrifugal distortion constants obtained by standard least squares fits based on the rigid rotor/centrifugal distortion model.[7] The centrifugal distortion constants for the ground state (*cf.* Table 10) have been kept fixed at their ground state values in all the remaining fits. This procedure is justified by the actual goodness of these fits (*cf.* the standard error cited at the bottom of the tables, which should

Table 9. Rotational constants (MHz) and inertial defects (uÅ^2) (I.D. $= I_c - I_a - I_b$)[a]

Molecule/state	A	B	C	ID
Parent, G.S.[b]	4234.7556(13)	1677.60185(87)	1201.58046(81)	0.00359(16)
$v_a = 1$	4223.6115(15)	1676.84772(89)	1202.50119(84)	−0.76881(15)
$v_a = 2$	4212.7454(24)	1676.0595(13)	1203.41205(56)	−1.53129(33)
$v_s = 1$	4232.4713(19)	1675.8359(11)	1202.03472(92)	−0.53721(22)
$v_s = 2$	4230.1801(11)	1674.09777(69)	1202.44316(66)	−1.05780(12)
$v_a' = 1$	4233.7674(20)	1668.5049(10)	1195.4475(10)	0.49104(19)
3,4D$_2$,G.S.	3860.2278(22)	1653.90721(92)	1157.83237(89)	0.00100(18)

[a] $I_a = 505376/A$ *etc.*   [b] G.S.: vibrational ground state.

Table 10. Centrifugal distortion constants [a] for the parent molecule (kHz).

Δ_J	Δ_{JK}	Δ_K	δ_J	δ_K
0.0618(25)	0.1225(41)	0.319(26)	0.01784(32)	0.1600(62)

[a] According to Watson.[9]

be comparable to the uncertainty of the frequencies, provided the model is perfect).

The stark effect of the $2_{20} - 3_{31}$ transition has been analysed to give the electric dipole moment (*cf.* Table 11). The value determined agrees very well with calculated values.[10]

The crucial question regarding the observed excited states is whether they correspond to separate vibrational modes as we have tacitly assumed above, or whether they are vibrational levels of increasing quantum number of a bell-clapper vibration. We believe that the last possibility can be definitely ruled out for the following reasons: (*i*) A potential which would reproduce the observed energy level pattern is almost inconceivable. (*ii*) To two of the excited states we have been able to assign the corresponding doubly excited states, as was mentioned above. The fact that we have not been able to assign the $v_a' = 2$ state is not very disturbing in this connection, since we know already that it cannot belong to the v_a manifold, $v_a = 2$ having been assigned. (*iii*) The differences $A_0 - A_k$ *etc.* and $(I.D.)_0 - (I.D.)_k$ of Table 12 depend linearly to within a few per cent on the vibrational quantum numbers, which is a strong indication of harmonic behaviour (see

below). (This conclusion has of course not been confirmed for the v_a' states.) (*iv*) The inertial defect is negative for two of the fundamental vibrational states. For excited states of an in-plane vibration one would normally expect a positive inertial defect.

Having ruled out this possibility we now want to determine which, if any, of the states belong to the bell-clapper vibration.

Being antisymmetric with respect to the C_2 operation, *cf.* Fig. 3a. there are two possibilities: either v_a or v_a' are the quantum numbers to be associated with this vibration. Since the vibrations seem to be predominantly harmonic we are looking for two normal coordinates Q_a and Q_a' which would be expected to give rise to such low fundamental states (normal frequencies) as have been found. Model calculations based on rough estimates of the force constants suggest the possibilities of Fig. 3 for these and for Q_s. Clearly the "butterfly" vibration, Fig. 3c, and the Q_s motion, Fig. 3b, must be nearly degenerate, so if one is assumed

Table 11. Stark shifts $\Delta\nu$ (MHz) and derived dipole moments for the $2_{20} - 3_{31}$ transition.

M	Field strength V/cm 418.4[a]		499.0	
	$\Delta\nu$	μ	$\Delta\nu$	μ
0	−2.08	3.107	−3.015	3.136
1	−2.57	3.015	−3.725	3.043
2	−4.57	3.071	−6.445	3.058
μ_{av}	3.07 ± 0.04 D			

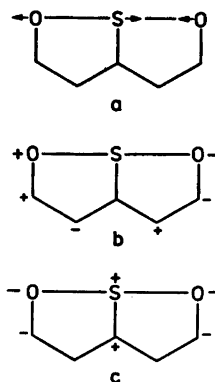[a] Obtained by calibration on COS with $\mu = 0.71521$ D.[9]

Fig. 3. Tentative normal coordinates for the three lowest modes: (a) The "bell-clapper" vibration, (b) the Q_s vibration, (c) the "butterfly" vibration, (see text).

Table 12. Differences between ground state values and excited state values divided by the vibrational quantum number.

v_k	$(A_0 - A_k)/v_k$	$(B_0 - B_k)/v_k$	$(C_0 - C_k)/v_k$	$(\mathrm{ID}_0 - \mathrm{ID}_k)/v_k$
$v_a = 1$	11.1441	0.7541	-0.9207	-0.76881
$v_a = 2$	11.0010	0.7712	-0.9158	-0.77044
$v_s = 1$	2.2843	1.7659	-0.4543	-0.53721
$v_s = 2$	2.2878	1.7520	-0.4313	-0.53070
$v_a' = 1$	0.9882	9.0970	6.1330	0.48745

to be low, the other is too. Normally the butterfly vibration is one of the lowest in fused ring systems like naphthalene, where it is located at 176 cm⁻¹, significantly lower than in the present case.[11] In conclusion: we believe that the coordinates of Fig. 3 are the most likely candidates for the low frequency modes.

Assuming this interpretation Q_a and Q_a', must now be coupled by Coriolis interaction. This implies that the sign of the inertial defect cannot be trusted as an indicator of whether a vibration is in-plane or not. Indeed the force-field calculations mentioned above suggest that the lowest of the two should have negative inertial defect whether it is in-plane or not.

Therefore, we cannot decide unambiguously whether the bell-clapper motion or the butterfly motion is the lowest.

Provided the assignments made above are essentially correct Q_s is of A_2 symmetry in the C_{2v} point group. Therefore it is forbidden in infrared absorption. The far infrared spectrum in the solid state shows two pronounced absorption peaks at 204 and 268 cm⁻¹ and only weak absorption in between. The Q_s vibration is allowed in Raman and the strongest peak is found at 238 cm⁻¹ (from the Rayleigh line) thus corroborating the term values of Table 8 as well as the considerations above.

DISCUSSION

There are several ways in which double minimum potentials are known to manifest themselves in molecular spectra: (*i*) By direct transitions between near degenerate levels when the central potential hump is fairly high, and when such transitions are allowed, as in ammonia and similar systems (*cf.* Ref. 12 for a review). (*ii*) By irregular spacings between

vibrational levels as in aniline, *p*-fluoro-aniline and similar molecules.[13] (*iii*) By a nonlinear (zig-zag) dependence of the rotational constants on the vibrational quantum numbers, as in ring-puckering molecules (*cf.* Ref. 14 for a review).

None of these effects have been observed in the present case: Ad (*i*) and (*ii*): Practically all lines of an intensity greater than 20 % of that of the corresponding lines in the ground state have been (or can be) assigned as described above, leaving no room for vibrational levels closer to the ground state than say 200 cm⁻¹. Considering the rather heavy mass of the sulfur atom this implies that if there is a hump at all then it must be very low, and most likely there is no such hump. We have already commented on (*iii*) above.

All evidence is in favour of the simplest possible assumption concerning the structure of 1,6-dioxa-6aλ⁴-thiapentalene, namely that it is a single minimum structure. It remains to say that the very small, positive inertial defect leaves no serious doubt as to the planarity of the system.

We would like to conclude this paper with a few remarks on the intramolecular forces. Comparison with naphthalene (see above) makes it most likely that the fundamental at 211 cm⁻¹ is to be associated with the butterfly vibration. Then 277 cm⁻¹ is to be associated with the bell-clapper vibration, implying that the corresponding potential is in fact rather steep. Assuming that this vibration can be considered as an exclusive motion of the sulfur atom, in a harmonic potential with force constant f, we obtain $f = 1.45$ mdyn/Å (145 N/m) corresponding to a classical amplitude in the ground state of *ca.* 1/20 of the S−O bond length.

REFERENCES

1. Gleiter, R. and Hoffmann, R. *Tetrahedron* 24 (1968) 5899.
2. a. Pedersen, C. Th. In Snyder, J. P., Ed., *Nonbenzenoid Aromatics*, Academic, New York, Vol. 3. *In press*; b. Gleiter, R. and Gygax, R. *Top. Current Chem. 63* (1976) 49.
3. Gelius, U., Basilier, E., Svensson, S., Bergmark, T. and Siegbahn, K. *J. Electron Spectrosc. 2* (1974) 405, 985.
4. Shen, Q. and Hedberg, K. *J. Am. Chem. Soc. 96* (1974) 289.
5. Corkill, M. J., Cox, A. P. and Ewart, I. C. *Chem. Commun.* (1976) 546.
6. Reid, D. H. and Webster, R. G. a. *J. Chem. Soc. Perkin Trans. 1* (1975) 2097; b. *Chem. Commun.* (1972) 1283; c. *J. Chem. Soc. Perkin Trans. 1* (1975) 775.
7. Gordy, W. and Cook, R. L. *Microwave Molecular Spectra*, Interscience, Chichester – New York 1970.
8. Watson, J. K. G. *J. Chem. Phys. 45* (1966) 1360.
9. Muenter, J. S. *J. Chem. Phys. 48* (1968) 4544.
10. Palmer, M. H. and Findlay, R. H. *J. Chem. Soc. Perkin Trans. 2* (1974) 1885.
11. Mitra, S. S. and Bernstein, H. J. *Can. J. Chem. 37* (1959) 553.
12. Wollrab, J. E. *Rotational Spectra and Molecular Structure*, Academic, London – New York 1967.
13. Larsen, N. W., Hansen, E. L. and Nicolaisen, F. M. *Chem. Phys. Lett. 43* (1976) 584.
14. Kroto, H. W. *Molecular Rotation Spectra*, Wiley, Chichester – New York 1975.