Microwave Spectrum of Cyclopentene-3,5-dione

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The microwave spectra of cyclopentene-3,5-dione in the ground state and the first four excited states of the ring bending vibration have been studied in the frequency region 26.5 to 40.0 GHz and the corresponding rotational constants have been determined. The ground state spectrum of one isotopically substituted species, 4-deuteriocyclopentene-3,5-dione, has also been assigned. The following values of the ground state rotational constants (MHz) were obtained from the spectra:

	unsubstituted species	4-deuterio species
A	6668.970 ± 0.003	6354.794 ± 0.007
B	2202.614 ± 0.002	2195.611 ± 0.004
C	1673.893 ± 0.002	1657.454 ± 0.004

From intensity and inertial-defect considerations the ring configuration was shown to be planar in the ground state. In addition, the nearly straight-line behaviour of the rotational constants as functions of the ring-puckering vibrational quantum number indicates that the ring-puckering vibration is nearly harmonic with a fundamental frequency of approximately 90 cm^{-1}.

The electric dipole moment for the unsubstituted species in the vibrational ground state was found to be 1.680 ± 0.009 Debye units.

Introduction

Considerable attention and inquiry has been focused upon conformations and ring-puckering vibrations in four-membered and pseudo four-membered ring molecules. With a pseudo four-membered ring molecule, we mean a five-membered ring molecule where one of the bonds has a much higher torsional rigidity than the others so that the pseudorotation [1, 2], normally present in five-membered rings, is hindered. In the case of cyclopentene-3,5-dione (4-cyclopentene-1,3-dione) the rigidity is caused by the presence of a double bond in the molecule. As a result of torsional motion hindrance around the double bond there remains only one low frequency, large amplitude, ring-puckering vibration in the molecule, while the ring-twisting vibration (involving a twist of the double bond) will have a much higher frequency.

The equilibrium configuration of four-membered or pseudo four-membered ring molecules is thought to be the result of a balance between ring strain and torsional forces around the bonds. Thus, ring strain tends to keept the molecule planar, while the torsional forces tend to favour a conformation in which the hydrogens on adjacent carbon atoms are staggered. In some molecules, the ring-angle strain is dominant and the molecule is effectively planar. In others, the torsional forces resulting from eclipsed hydrogens dominate and lead to a non-planar equilibrium structure with a potential energy maximum present at the planar conformation.

On the basis of these arguments, one would expect a molecule like cyclopentene-3,5-dione with no eclipsing methylene groups to be planar. Other factors that would also tend to favour a planar ring structure are the approximate sp^2-hybridization of the carbonyl carbon atoms and the possible existence of a small amount of hyperconjugation. In order to confirm and extend the knowledge of these and other factors contributing to equilibrium conformations and ring-puckering vibrations in such molecules, further experimental studies will be valuable.

Experimental

A sample of cyclopentene-3,5-dione was obtained from Aldrich-Europe and used without further purification. The deuterium-substituted species, 4-deuteriocyclopentene-3,5-dione, was prepared by exchange of cyclopentene-3,5-dione with D_2O in

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ethanol. In this way, a mixture of undeuterated, mono-4-deuterated and di-4,4-deuterated cyclopentene-3,5-dione was obtained with the monodeuterated species dominating.

The microwave spectra were recorded using a Hewlett-Packard Model 8460 A spectrometer equipped with a phase-stabilized source oscillator and with a Stark cell modulation frequency of 33.33 kHz. The measurements were carried out at room temperature in the R-band region of 26.5 to 40.0 GHz and with sample pressures from 20 to 60 mTorr (2.7 to 8 Pa). The measurements of the Stark effect used in the dipole moment determinations had to be performed in the K-band region of 18.0 to 26.5 GHz.

Microwave Spectrum

The molecule is a near-prolate symmetric top with $\varkappa = -0.79$. Only b-type transitions were observed in the spectrum which was dominated by a large number of strong Q-branch transitions belonging to the families $J_{K,J-K} \leftarrow J_{K-1,J-K+1}$ with K-values ranging from 1 to 6 and $J_{K,J-K+1} \leftarrow J_{K-1,J-K+2}$ with K from 2 to 4. In both families, the J-values ranged from 6 to 28. The R-branch lines were much less numerous and weaker in intensity. No c-type transitions were observed in the spectrum which is consistent with a nearly planar molecule in the ground state.

A special computer program written by the authors was found to be a very convenient aid in the assignment of the ground and first excited state Q-branch transitions. This program is similar to one of the programs described by van Eijck [3] and is based on the following principles: Two selected strong Q-lines in the calculated spectrum are successively identified with all possible pairs of strong lines in the observed spectrum. The spectrum calculated on the basis of each of these tentative assignments is compared to the experimental spectrum. Finally, the values of $A - C$ and $\varkappa$ that give the best fit are written out by the program. Once the ground and first excited state lines had been assigned, the lines belonging to the higher excited states of the ring-puckering vibration were easily identified since they are situated at almost equidistant frequencies. Once approximate values of the constants $A - C$ and $\varkappa$ had been obtained from two Q-lines the other Q-lines could be identified successively by improving the constants after each additional line. The R-branch lines were identified from calculations with the constant $A + C$ estimated from preliminary structural data. No lines were assigned by means of their Stark effects since the Stark intensities were too weak in the actual cases.

Table 1 shows the observed frequencies and assignments of the lines used in the least squares method for fitting the molecular constants in the $v = 0$ to 4 states. The measurements of the spectra were carried out in the frequency region 26.5 to 40.0 GHz and extension of the measurements into other bands was not considered profitable in order to further improve the rotational constants. Extension to the K-band region was, however, necessary for the dipole moment determinations. A Watson first-order centrifugal distortion analysis [4] was included in the fittings when determining the rotational constants. The resulting molecular constants for the different vibrational states obtained from the fittings are tabulated in Table 2.

Molecular Planarity and Ring-Puckering Vibration

Figure 1 shows how the rotational constants of cyclopentene-3,5-dione vary with the ring-puckering quantum number, v. For a perfectly harmonic vibration, these curves would be straight lines. This is almost true for the experimental curves although a very slight convexity is observed. According to previous experience [5], this convexity would indicate a potential function with walls slightly steeper than a harmonic function. The absence of even the slightest tendency towards zig-zagging in these curves is conclusive evidence that a possible barrier present at the planar configuration must either be practically zero or sufficiently high to yield a permanent non-planar conformation. Even a very small barrier at the planar form, much lower than the zero-point vibrational level, will give rise to an observable zig-zag behaviour of the rotational constants. A permanent non-planar conformation is contradicted by the experimental value of the inertial defect, by the relative intensities of the absorption lines, and by the fact that 4-deuterio-cyclopentene-3,5-dione was found to produce only a single microwave spectrum.

Figure 2 shows how the inertial defect, $\Delta = I_c - I_a - I_b$, varies with the quantum number v for

Table 1. Assigned rotational transitions with frequencies (MHz) for the ground state and the $v = 1-4$ excited states of the ring-bending vibration of cyclopentene-3,5-dione.

Transition	Ground state		$v = 1$		$v = 2$		$v = 3$		$v = 4$	
	ν_{obs}	$\nu_{obs} - \nu_{calc}$	ν_{obs}	$\nu_{obs} - \nu_{calc}$	ν_{obs}	$\nu_{obs} - \nu_{calc}$	ν_{obs}	$\nu_{obs} - \nu_{calc}$	ν_{obs}	$\nu_{obs} - \nu_{calc}$
$3_{30} \leftarrow 2_{21}$	35311.73	−0.09								
$3_{31} \leftarrow 2_{20}$	35265.29	0.01								
$5_{24} \leftarrow 4_{13}$	30923.03	0.04								
$7_{26} \leftarrow 6_{15}$	35869.10	0.02								
$8_{08} \leftarrow 7_{17}$	27691.47	0.01	27764.92	0.02	27836.82	0.00	27907.46	0.00	27977.15	0.00
$8_{18} \leftarrow 7_{07}$	29152.29	−0.06								
$8_{27} \leftarrow 7_{16}$	38092.49	0.00	38050.73	−0.01						
$9_{09} \leftarrow 8_{18}$	31310.98	−0.01	31388.08	0.02			31537.82	−0.02		
$9_{18} \leftarrow 8_{27}$	29403.52	0.03								
$9_{19} \leftarrow 8_{08}$	32231.63	0.00	32287.52	−0.03	32342.63	0.00	32397.19	0.02		
$10_{0,10} \leftarrow 9_{19}$	34834.72	0.02	34916.52	0.00	34996.62	−0.04				
$10_{1,10} \leftarrow 9_{09}$	35399.27	−0.01	35466.72	0.00	35533.06	0.04				
$11_{0,11} \leftarrow 10_{1,10}$	38292.62	0.02								
$12_{2,10} \leftarrow 11_{39}$	36171.01	−0.02								
$6_{42} \leftarrow 6_{33}$	32789.96	0.02								
$7_{43} \leftarrow 7_{34}$	32505.28	−0.06								
$8_{44} \leftarrow 8_{35}$	32030.74	0.04								
$9_{45} \leftarrow 9_{36}$	31305.02	0.00								
$9_{46} \leftarrow 9_{37}$	33056.28	0.03								
$10_{38} \leftarrow 10_{29}$	28218.77	0.01	28047.20	−0.01	27880.81	0.01				
$10_{46} \leftarrow 10_{37}$	30293.26	−0.01	30007.50	−0.03						
$10_{47} \leftarrow 10_{38}$	33256.68	0.00								
$11_{1,10} \leftarrow 11_{0,11}$	29800.48	0.00								
$11_{2,10} \leftarrow 11_{1,11}$	32124.80	−0.01								
$11_{39} \leftarrow 11_{2,10}$	29861.32	0.00								
$11_{47} \leftarrow 11_{38}$	29015.66	0.00	28726.77	0.00	28445.41	0.01	28170.73	−0.04		
$11_{48} \leftarrow 11_{39}$	33614.41	−0.07								
$12_{3,10} \leftarrow 12_{2,11}$	31788.75	0.00	31624.49	0.00						
$12_{48} \leftarrow 12_{39}$	27565.32	0.04			26999.78	−0.01				
$12_{49} \leftarrow 12_{3,10}$	34173.11	0.02	33927.40	−0.01						
$13_{1,12} \leftarrow 13_{0,13}$	37102.37	−0.02	36977.29	0.01						
$13_{2,12} \leftarrow 13_{1,13}$	38154.55	0.02								
$13_{3,11} \leftarrow 13_{2,12}$	33985.79	0.00								
$13_{4,10} \leftarrow 13_{3,11}$	34971.10	0.03								
$14_{2,12} \leftarrow 14_{1,13}$	30711.07	0.04								
$14_{3,12} \leftarrow 14_{2,13}$	36427.63	−0.03	36266.28	0.01						
$14_{4,11} \leftarrow 14_{3,12}$	36038.73	0.00	35810.22	0.00			32591.57	0.03		
$14_{59} \leftarrow 14_{4,10}$					38026.08	−0.01	37665.49	0.03		
$15_{2,13} \leftarrow 15_{1,14}$			34729.25	−0.03						
$15_{4,12} \leftarrow 15_{3,13}$	37395.72	0.01	37176.76	0.05	36964.66	−0.02				
$15_{5,10} \leftarrow 15_{4,11}$	37300.08	−0.01	36912.63	0.00	36534.86	0.02				
$16_{5,11} \leftarrow 16_{4,12}$	35570.04	0.00	35179.16	0.00	34798.37	0.01				
$17_{3,14} \leftarrow 17_{2,15}$	30422.18	0.06	30420.58	0.07						
$17_{5,12} \leftarrow 17_{4,13}$	33714.30	0.01	33329.75	−0.01			32591.57	0.03		

Table 1 (continued)

Transition	Ground state ν_{obs}	Ground state $\nu_{obs}-\nu_{calc}$	$v=1$ ν_{obs}	$v=1$ $\nu_{obs}-\nu_{calc}$	$v=2$ ν_{obs}	$v=2$ $\nu_{obs}-\nu_{calc}$	$v=3$ ν_{obs}	$v=3$ $\nu_{obs}-\nu_{calc}$	$v=4$ ν_{obs}	$v=4$ $\nu_{obs}-\nu_{calc}$
$18_{3,15} \leftarrow 18_{2,16}$	34554.56	−0.04	34552.87	−0.06						
$18_{5,13} \leftarrow 18_{4,14}$	31925.72	−0.04	31560.77	0.03						
$19_{4,15} \leftarrow 19_{3,16}$	27261.57	0.02	27208.98	−0.01	27161.74	−0.02	27119.43	0.00		
$19_{5,14} \leftarrow 19_{4,15}$	30428.84	0.02	30097.71	0.00	29777.86	−0.01				
$20_{4,16} \leftarrow 20_{3,17}$	30102.38	0.00								
$20_{5,15} \leftarrow 20_{4,16}$	29442.01	−0.01	29158.18	−0.01			28623.21	0.02	28370.58	−0.03
$21_{4,17} \leftarrow 21_{3,18}$	33663.33	0.00					33732.57	−0.01		
$21_{5,16} \leftarrow 21_{4,17}$	29148.20	0.01	28922.17	−0.01	28706.90	−0.02	28501.54	−0.02	28305.55	0.00
$22_{4,18} \leftarrow 22_{3,19}$	37787.40	−0.02	37824.70	0.01	37863.60	0.01	37903.37	0.02		
$22_{5,17} \leftarrow 22_{4,18}$	29678.94	0.02	29517.58	−0.01	29366.27	0.05	29224.00	−0.03	29090.54	0.08
$22_{6,16} \leftarrow 22_{5,17}$							38030.18	−0.04	37582.44	0.02
$23_{5,18} \leftarrow 23_{4,19}$	31109.91	−0.11	31016.00	0.00	30930.82	0.02	30853.71	0.02		
$23_{6,17} \leftarrow 23_{5,18}$	37401.41	0.00	36946.67	0.01	36506.82	0.00	36080.85	0.00	35667.73	−0.05
$24_{5,19} \leftarrow 24_{4,20}$	33457.21	−0.01	33427.98	−0.02	33406.04	−0.02	33390.70	−0.04	33381.62	−0.03
$24_{6,18} \leftarrow 24_{5,19}$	35753.16	0.00	35349.94	−0.02	34962.15	−0.02				
$25_{5,20} \leftarrow 25_{4,21}$	36667.88	0 03	36694 64	0.00	36726.83	0.01				
$25_{6,19} \leftarrow 25_{5,20}$	34732.02	0.00	34397.37	−0.01	34078.13	0.00	33773.24	0.01	33481.81	0.07
$26_{6,20} \leftarrow 26_{5,21}$	34519.90	0.01	34266.45	−0.01	34027.84	0.00	33803.00	0.03	33591.05	−0.04
$27_{6,21} \leftarrow 27_{5,22}$	35240.01	0.00	35075.17	0.02	34923.94	0.03				
$28_{6,22} \leftarrow 28_{5,23}$	36952.28	0.03	36877.22	0.00	36814.03	−0.03				

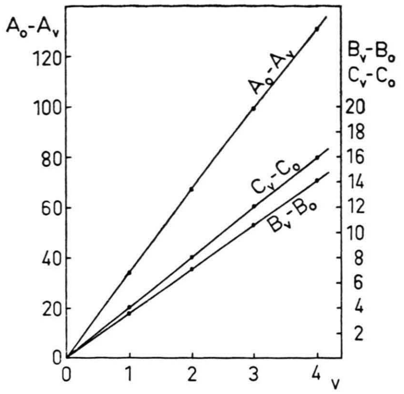

Fig. 1. Variation of the rotational constants (MHz) of cyclopentene-3,5-dione as a function of the ring-bending vibrational quantum number, v.

the ring-puckering vibration. The rapid decrease of the intertial defect with increasing v is typical for an out-of-plane vibration. The extrapolated value of Δ in the hypothetical vibrationless state with $v=-1/2$ is -2.932 a.m.u. Å^2. A correction using 3.195 a.m.u. Å^2 for the protruding methylene hydrogens yields 0.263 a.m.u. Å. This is a small positive value typical for a planar molecule of this size. For comparison, it may be mentioned that the corresponding value for cyclopentene-4-one after correction for the methylene hydrogens amounts to 0.282 a.m.u. Å^2 [6].

Starting from the well-known expression of Oka and Morino [7] for the inertial defect of a planar molecule, Hanyu et al. [8] have derived the following equation for the fundamental frequency of an out-of-plane vibration and the change of the inertial defect between the ground vibrational and

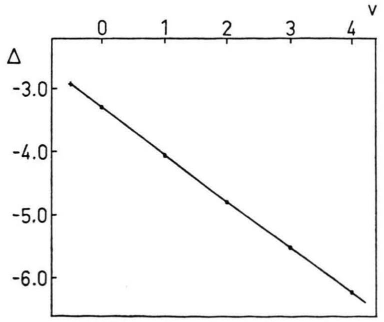

Fig. 2. Variation of the inertial defect, $\Delta = I_c - I_a - I_b$ (a.m.u. Å^2), of cyclopentene-3,5-dione as a function of the ring-bending vibrational quantum number, v.

Table 2. Rotational constants (MHz), principal moments of inertia (a.m.u. Å^2)[a] and centrifugal distortion coefficients (Hz) for the ground state and the $v = 1$ to 4 excited states of the ring-bending vibration of cyclopentene-3,5-dione.

	Ground State	$v = 1$	$v = 2$	$v = 3$	$v = 4$
A	6668.970 ± 0.003	6634.868 ± 0.004	6601.753 ± 0.006	6569.470 ± 0.013	6538.082 ± 0.025
B	2202.614 ± 0.002	2206.204 ± 0.003	2209.754 ± 0.005	2213.248 ± 0.011	2216.740 ± 0.005
C	1673.893 ± 0.002	1677.982 ± 0.003	1682.000 ± 0.005	1685.932 ± 0.011	1689.853 ± 0.004
$\varkappa$	−0.788	−0.787	−0.785	−0.784	−0.783
I_a	75.78067 ± 0.00003	76.17016	76.55224	76.92842	77.29775
I_b	229.4451 ± 0.0002	229.0718	228.7037	228.3427	227.9830
I_c	301.9183 ± 0.0003	301.1827	300.4631	299.7624	299.0669
$\Delta = I_c - I_a - I_b$	−3.3075	−4.0593	−4.7928	−5.5087	−6.2139
Δ_J	98 ± 9	95 ± 19	144 ± 25	20 ± 71	98
Δ_{JK}	152 ± 13	166 ± 18	82 ± 36	154 ± 50	152
Δ_K	2304 ± 156	2140 ± 173	2802 ± 299	1537 ± 433	1830 ± 539
δ_J	24.7 ± 0.6	27.0 ± 0.7	26.0 ± 1.2	29.6 ± 1.7	24.7
δ_K	310 ± 17	235 ± 19	261 ± 39	173 ± 52	140 ± 69

[a] Conversion factor $BI = 505379$ MHz a.m.u. Å^2.

first excited state of the same vibration:

$$\begin{aligned}\nu &= (h/2\pi^2 c)/(\Delta_0 - \Delta_1)\\ &= 67.431/(\Delta_0 - \Delta_1)\ \text{cm}^{-1}\,.\end{aligned}$$

Upon deriving this formula, it was assumed that all in-plane vibrations are sufficiently high in frequency to make their interaction with the out-of-plane vibration negligible. The interaction of the latter with other out-of-plane vibrations is always zero since the corresponding Coriolis coupling coefficients vanish. Although the formula was originally derived for strictly planar molecules, it will nevertheless hold fairly well for molecules such as cyclopentene-3,5-dione where all the heavy atoms are situated in one plane, as we shall establish below. In the studied molecule where $\Delta_0 - \Delta_1 = 0.752$ a.m.u. Å^2, the formula yields $\nu = 89.7$ cm^{-1} for the ring-puckering vibration.

If the barrier at the planar configuration were high, resulting in a puckered equilibrium configuration, the intensities of the rotational transitions in the different vibrational states would only depend on their respective populations. Otherwise, in the case of a low or non-existent barrier, the nuclear-spin statistical weight factors must also be considered. In the expected planar configuration of cyclopentene-3,5-dione, a twofold rotation about the b principal axis ($C_2{}^b$) will exchange two pairs of equivalent protons with spin 1/2. Then the total molecular wave function must be symmetric with respect to this operation. Also, the ring-puckering vibration is antisymmetric with respect to $C_2{}^b$ which means that the vibrational wave function must be symmetric with respect to $C_2{}^b$ for even v values and antisymmetric for odd v values. The rotational states (ee, oo) are symmetric with respect to $C_2{}^b$ and will therefore have to be combined with the 10 symmetric nuclear-spin functions for even v values and with the 6 antisymmetric nuclear-spin functions for odd v values. The reverse will be true for the antisymmetric rotational states (eo, oe).

The experimental results were in perfect agreement with the weight factors calculated on the basis of the above argument. Thus, in a great many cases, rotational transitions belonging to an excited vibrational state were observed to have a higher intensity than the corresponding lines belonging to the next lower excited (or ground) state.

On the basis of these findings we can exclude the high-barrier alternative. In agreement with the results of the inertial-defect determinations, the intensity distribution of the spectral lines indicates that the studied molecule has a planar equilibrium configuration.

After correction for the nuclear-spin statistical weight factors, intensity measurements on a number of isolated absorption lines at 20 °C yielded an average intensity ratio of 0.637 between the first excited state of the ring-puckering vibration and the ground state. Using Boltzmann's distribution law, this corresponds to an energy difference of 92 ± 34 cm^{-1} which is in fair agreement with the value calculated from the variation of the inertial defect.

Isotopic Species and Molecular Geometry

In order to gain further structural information about the molecule, the microwave spectrum of the 4-deuteriocyclopentene-3,5-dione species was recorded. The transitions are given in Table 3, together with their differences from those calculated in a least squares analysis. The corresponding molecular constants are recorded in Table 4.

The r_s-coordinates for the hydrogen atoms on C_4 referred to the principal inertial axis system of the parent molecule can thus be determined from Kraitchman's equations [9, 10] for a non-planar asymmetric rotor:

$$a^2 = \frac{1}{2\mu}\left[(I_b' - I_b) + (I_c' - I_c) - (I_a' - I_a)\right] \times \left[1 + \frac{(I_a' - I_a) - (I_b' - I_b) + (I_c' - I_c)}{2(I_a - I_b)}\right] \times \left[1 + \frac{(I_a' - I_a) + (I_b' - I_b) - (I_c' - I_c)}{2(I_a - I_c)}\right]$$

where $\mu = \Delta m M/(\Delta m + M)$ and I', I and Δm are respectively the moments of intertia of the isotopic species, the moments of intertia of the unsubstituted species, and the change in the mass, M, of the parent molecule upon isotopic substitution. Analogous expressions for the b and c coordinates can be obtained by cyclic permutation of the subscripts. The r_s-coordinates so calculated for the hydrogens on C_4 are $b = 1.7280 \pm 0.0006$ Å and $c = 0.8808 \pm 0.0007$ Å. The coordinate a cannot be determined from Kraitchman's equations but for symmetry reasons it is obviously equal to zero.

Table 3. Assigned rotational transitions with frequencies (MHz) of 4-deuteriocyclopentene-3,5-dione in the vibrational ground state.

Transition	ν_{obs}	$\nu_{obs} - \nu_{calc}$
$9_{09} \leftarrow 8_{18}$	31080.89	0.04
$9_{19} \leftarrow 8_{08}$	31797.58	0.00
$10_{0,10} \leftarrow 9_{19}$	34538.46	−0.02
$10_{1,10} \leftarrow 9_{09}$	34964.65	−0.05
$11_{0,11} \leftarrow 10_{1,10}$	37939.86	0.03
$11_{48} \leftarrow 11_{39}$	31679.49	0.00
$12_{57} \leftarrow 12_{48}$	37790.06	−0.04
$13_{58} \leftarrow 13_{49}$	36793.61	0.02
$15_{4,12} \leftarrow 15_{3,13}$	35977.08	0.00
$16_{5,12} \leftarrow 16_{4,13}$	39918.53	0.02
$17_{3,14} \leftarrow 17_{2,15}$	31306.65	0.00
$17_{4\,14} \leftarrow 17_{3,15}$	39885.82	−0.01
$17_{5,12} \leftarrow 17_{4,13}$	30291.26	0.01
$18_{3,15} \leftarrow 18_{2,16}$	35509.67	−0.01
$20_{4,16} \leftarrow 20_{3,17}$	31006.74	0.02
$21_{6,15} \leftarrow 21_{5,16}$	37102.70	0.00
$23_{5,18} \leftarrow 23_{4,19}$	31264.50	−0.01
$23_{6,17} \leftarrow 23_{5,18}$	33455.10	0.00
$24_{5,19} \leftarrow 24_{4,20}$	34407.28	0.00
$24_{6,18} \leftarrow 24_{5,19}$	32463.58	0.01
$25_{6,19} \leftarrow 25_{5,20}$	32299.74	−0.02

Table 4. Rotational constants (MHz), principal moments of inertia (a.m.u. Å^2)[a] and centrifugal distortion coefficients (Hz) of 4-deuteriocyclopentene-3,5-dione in the vibrational ground state.

A	6354.794	± 0.007
B	2195.611	± 0.004
C	1657.454	± 0.004
$\varkappa$	−0.771	
I_a	79.52721	± 0.00009
I_b	230.1769	± 0.0004
I_c	304.9129	± 0.0008
Δ_J	70	± 21
Δ_{JK}	167	± 23
Δ_K	2331	± 217
δ_J	26.5	± 1.2
δ_K	236	± 31

[a] Conversion factor $BI = 505379$ MHz a.m.u. Å^2.

These results together with the rotational constants of the unsubstituted species can be used in order to deduce some information about the molecular geometry. Of course, such information that is obtained from just two spectra will be of preliminary nature. By assuming reasonable values for most of the molecular parameters from analogies with other molecules, the remaining parameters can be fitted to the experimental constants. Such assumed parameters for cyclopentene-3,5-dione are shown in Table 5. The only remaining parameter consists of $\angle C_1C_2C_3$. By fitting this angle to the rotational constants and to the b and c coordinates of the hydrogens bonded to C_4, values ranging from 109° to 113° were obtained. Actually, the calculated

Table 5. Molecular parameters assumed for cyclopentene-3,5-dione.

$C_1{=}C_2$	1.34 Å
$C_2{-}C_3$	1.44 Å
$C_3{-}C_4$	1.52 Å
$C{=}O$	1.21 Å
$C_1{-}H$	1.08 Å
$C_4{-}H$	1.09 Å
$\angle C_2C_3O = \angle C_4C_3O$	
$\angle (C_5C_1C_2C_3) - (C_3C_4C_5)$	180° (planar ring)
$\angle C_1C_2H$	124.7°
$\angle HC_4H$	108.0°

constants A, B, C, $b(\mathrm{H4})$ and $c(\mathrm{H4})$ were more sensitive to a variation in $\angle C_1C_2C_3$ than to reasonable variations in the parameters in Table 5. This also gives confirmation to the already mentioned estimated value for $\angle C_1C_2C_3$.

Dipole Moment

No suitable line for Stark effect measurements could be found in the R-band region. In some cases this resulted from the weakness of prospective lines, but mostly from the rich abundance of vibrational satellites yielding crowed regions with many overlaps in the spectrum.

After a thorough search in the K-band region, the $3_{22} \leftarrow 2_{11}$ line at 25028.56 MHz proved to be the only suitable one for dipole moment determinations. The Stark shifts, $\Delta\nu$, for the $M = 1$ and 2 components of this line were found to be strictly proportional to the square of the applied electric field, E^2, up to at least 1100 V cm^{-1}.

The guide spacing of the Stark cell was calibrated using the $J = 2 \leftarrow 1$, $\Delta M = 0$ transition at 24325.92 MHz in the vibrational ground state of the normal species of OCS with $\mu = 0.71521$ Debye units [11].

The values for $\Delta\nu/E^2$ for the two M-components $M = 1$ and 2 of the $3_{22} \leftarrow 2_{11}$ line were determined to be 8.933×10^{-6} and 33.933×10^{-6} MHz V^{-2} cm^2 thus yielding $\mu_b = 1.678$ and 1.682 Debye units, respectively. Since the dipole moment, μ, is restricted by symmetry to lie along the b-axis $\mu = \mu_b = 1.680 \pm 0.009$ Debye units. This value is in reasonable agreement with results of dipole moment determinations of cyclopentene-3,5-dione in benzene, which gave 1.80 Debye units [12].

The experimental value of the dipole moment is actually significantly larger than the one that is calculated from reasonable bond moments (for instance, $\mu_{C=O} = 2.8$ to 3.0 Debye units [5, 6, 13]) and a structure like that in Table 5. The latter value will just be 0.6 to 1.0 Debye units when $\angle C_1C_2C_3$ is in the range 109° to 113°. Such an increase in the dipole moment from the calculated one, usually called the mesomeric moment, may be attributed to the charge transfer brought about through resonance interaction by means of delocalized orbitals from the ethylene group to the carbonyl groups, which is shown in Figure 3.

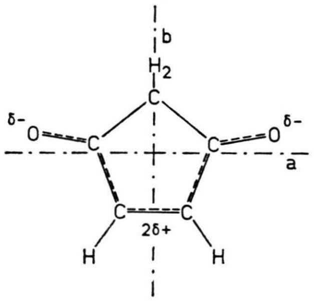

Fig. 3. Mesomeric contribution to the dipole moment of cyclopentene-3,5-dione. The orientation of the a and b principal axes is also indicated.

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