Structure and Potential Energy Function of Cyclopent-3-enone

Part 1.—Microwave Spectrum, Ring Planarity, r_s-structure, and Dipole Moment

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The microwave spectra of cyclopent-3-enone in the ground state, the first seven excited states of the ring bending vibration and with one quantum of the ring twisting mode excited have been assigned. A planar equilibrium configuration for the ring is established on the basis of several arguments.

The rotational spectra in the vibrational ground state of the six different singly substituted isotopic species, [2-D], [3-D], $[1^{13}C]$, $[2^{-13}C]$ and $[3^{-13}C]$, of cyclopent-3-enone have also been assigned, the first three in isotopically enriched samples and the latter three in natural abundance. The rotational constants determined from the spectra are :

| | parent | [¹⁸ O] | [2-D] | [3-D] | [1-13C] | [2-13C] | [3-13C] |
|-------|----------|--------------------|----------|---------|---------|---------|---------|
| A/MHz | 7378.32 | 7378.18 | 6951.27 | 7217.99 | 7378.68 | 7217.16 | 7332.10 |
| B/MHz | 3615,209 | 3421.510 | 3596.396 | 3473.83 | 3598.79 | 3615.07 | 3559.75 |
| C/MHz | 2503.587 | 2409.136 | 2460.956 | 2417.32 | 2495.77 | 2484.67 | 2471.66 |

The r_s -coordinates of each atom have been obtained from these constants. Two of the coordinates are small and their determination by other methods is discussed. The essentially r_s -structure reported is :

r(C r(C₃ r(∠C ∠ H

 $\begin{aligned} r(C_1-C_2) &= 1.524 \pm 0.008 \text{ Å}, \\ r(C_3-C_3') &= 1.338 \pm 0.004 \text{ Å}, \\ r(C=O) &= 1.210 \pm 0.002 \text{ Å}, \\ r(C_2-H_2) &= 1.086 \pm 0.004 \text{ Å}, \\ r(C_2-H_2) &= 1.086 \pm 0.004 \text{ Å}, \\ \angle C_2C_1C_2' &= 109^\circ 12' \pm 1^\circ \\ \angle C_1C_2C_3 &= 103^\circ 08' \pm 48', \\ \angle H_3C_3C_{3'} &= 124^\circ 42' \pm 16', \\ \end{aligned}$

The value of the electric dipole moment measured using the Stark effect is 2.79 ± 0.03 D.

The microwave and far infra-red spectra of four and five membered organic ring systems have recently been the subjects of intensive investigation.¹⁻¹⁶ The interest in these spectra originates in the possibilities that they present for the determination of the detailed geometrical structure of the ring and the quantitative form for the potential energy functions which govern low lying ring vibrations. Such molecular parameters are revealing of the balance between the various forces acting in the molecule, in particular the forces due to ring angle strain and the torsional forces about ring bonds. For example, in four and five membered rings, the planar ring configurations is favoured by resistance to further decrease of the already strained ring angles. However, the eclipsed configuration thereby required of any adjacent methylene groups in the ring is energetically unfavourable. In some molecules the ring angle strain factor is dominant and a planar or very nearly planar ring results (for example, trimethylene oxide,^{1, 2} cyclobutanone^{3, 4} 2,5-dihydrofuran,⁵ 3-methyleneoxetan ^{6, 7} cyclopent-2-enone⁸). For others (for example, trimethylene sulphide,^{4, 9} cyclopentene,¹⁰⁻¹² methylenecyclobutane^{13, 14} and cyclopentanone¹⁵), however, the

unfavourable energy of the eclipsed methylene groups dominates and leads to a definitely non-planar equilibrium ring structure with a potential energy maximum at the planar ring.

Cyclopent-3-enone (fig. 1) presents an example of the situation in which both factors favour a planar equilibrium ring structure, for then the ring angles are maximised and the C—H bonds on the adjacent methylenic and ethylenic carbon atoms are staggered. Moreover, cyclopent-3-enone is a particularly suitable molecule for which to determine quantitatively both the geometrical structure and the potential energy function governing the out-of-plane ring bending vibration. A simple, strong microwave spectrum and C_{2v} molecular symmetry make a complete r_s -structure feasible while the low frequency, ring bending vibration is separated enough from all



FIG. 1.-Inertial axes, ring atom numbering and structure of cyclopent-3-enone.

other molecular vibrations to validate the determination of a one dimensional potential function from both the vibrational satellites in the microwave spectrum and the far infra-red spectrum.

We have reported the microwave spectrum of the common isotopic variety of cyclopent-3-enone in a preliminary publication.¹⁶ We now report fully the microwave spectra of the parent molecule and of the six different, single isotopically substituted species and establish the equilibrium ring configuration, the r_s -structure and the electric dipole moment. In a further paper (Part 2) ¹⁷ we report the vibrational energy level separations associated with the ring bending vibration as determined from the far infra-red spectrum and corroborated by the microwave spectrum of the compound. The potential energy function for the ring-bending vibration is derived from the results.

EXPERIMENTAL

PREPARATION OF CYCLOPENT-3-ENONE

PARENT SPECIES $({}^{12}C_5H_6{}^{16}O)$.—Dicyclopentadienol (tricyclo[5,2,1,0^{2,6}]deca-4,8-dien-3-ol), prepared by the oxidation of dicyclopentadiene with selenium dioxide, ¹⁸ was pyrolysed at 140-150°C in an atmosphere of nitrogen to yield a mixture of cyclopent-3-enone and cyclopent-2-enone.¹⁹ The more abundant symmetrical isomer was efficiently separated from the thermodynamically more stable cyclopent-2-enone by g.l.c. using a 30 ft $\times \frac{3}{4}$ in. Carbowax 20 M column at 135°C. The sample was stored at dry-ice temperature to inhibit isomerisation but nevertheless further chromatographic purification was occasionally required.

[¹⁸O]CYCLOPENT-3-ENONE.—A method similar to that described for [¹⁸O]acetone ²⁰ was used. An excess of approximately 10^{-4} M solution of HCl in H₂¹⁸O, prepared by condensing HCl gas into H₂¹⁸O (98 atom % excess ¹⁸O), was allowed to react with cyclopent-3-enone for a few minutes at room temperature. Partial separation from the excess water was effected by distillation at dry-ice temperature. About 90 % enrichment in cyclopent-3-enone was thus achieved.

[2-D]CYCLOPENT-3-ENONE.—Dicyclopentadienol was shaken with excess D_2O (99.7 mol % excess) at room temperature and the D_2O then removed by azeotropic distillation with benzene. The [OD]dicyclopentadienol so produced was converted to cyclopent-3-enone. It is interesting that deuteration in the product was exclusively at the 2-position according to the microwave spectrum, a fact which is consistent with the mechanism proposed for the dicyclopentadienol pyrolysis by Hess and Brown.¹⁹

[3-D]CYCLOPENT-3-ENONE.—Deuterated dicyclopentadiene was prepared by heating 0.45 mol of freshly prepared cyclopentadiene, 27.5 mol of water (ratio $H_2O : D_2O = 4 : 1$)

| | | obs. | | obs. | | obs. | | obs. |
|------------------------------------|-----------|--------|---------------|--------|---------------|--------|---------------|-------|
| transition | obs. | -calc. | obs. | -calc. | obs. | -calc. | obs. | -calc |
| | ground | state | $V_{\rm B} =$ | = 1 | $V_{\rm B} =$ | - 2 | $V_{\rm B} =$ | 3 |
| $5_{0,5}-4_{0,4}$ | 27 635.14 | 0.01 | 27 704.37 | 0.02 | 27 769.91 | -0.01 | 27 833.02 | -0.01 |
| 5 _{1,5} -4 _{1,4} | 27 113.38 | 0.00 | 27 188.84 | -0.01 | 27 260.55 | 0.01 | 27 329.68 | 0.01 |
| 5 _{1,4} -4 _{1,3} | 32 171.06 | 0.02 | 32 229.27 | -0.01 | 32 284.72 | 0.01 | _ | |
| 52,3-42,2 | 33 062.47 | 0.00 | 33 130.90 | 0.00 | 33 196.70 | 0.00 | 33 260.81 | 0.00 |
| 52,4-42,3 | 30 124.25 | 0.01 | 30 192.58 | 0.00 | 30 257.75 | 0.02 | 30 320.79 | 0.02 |
| 53,2-43,1 | 31 593.35 | -0.05 | 31 666.90 | -0.03 | 31 737.59 | -0.04 | 31 806.45 | -0.03 |
| 53,3-43,2 | 31 093.30 | 0.01 | 31 163.26 | 0.03 | | | 31 295.25 | 0.04 |
| $6_{0,6}-5_{0,5}$ | 32 533.99 | -0.01 | 32 620.36 | 0.01 | 32 702.24 | 0.00 | 32 781.07 | -0.02 |
| 61,5-51,4 | 37 715.19 | -0.01 | 37 782.40 | -0.01 | 37 846.10 | 0.01 | 37 907.40 | -0.01 |
| 61.6-51.5 | 32 246,73 | 0.01 | 32 337.52 | 0.01 | 32 423.76 | 0.02 | 32 506.87 | 0.01 |
| 62,5-52,4 | 35 782.06 | 0.01 | 35 863.26 | 0.00 | 35 940.58 | -0.02 | 36 015.34 | 0.00 |
| 62.4-52.3 | 39 871.11 | 0.00 | 39 948.28 | -0.02 | | | | |
| 61.3-51.2 | 38 504.19 | -0.01 | 38 594.20 | -0.02 | 38 680.93 | -0.03 | 38 765.55 | -0.02 |
| 63.4-53.3 | 37 305.46 | 0.00 | 37 388.32 | 0.02 | 37 467.58 | -0.01 | 37 544.51 | 0.01 |
| 64.2-54.1 | 37 495,18 | -0.06 | 37 581.45 | -0.04 | | | 37 744.71 | -0.05 |
| 64.3-54.2 | 37 405.88 | 0.08 | 37 490.95 | 0.06 | 37 572.54 | 0.05 | 37 651.79 | 0.06 |
| 70.7-60.6 | 37 464.72 | 0.00 | 37 568.56 | 0.01 | 37 667.09 | 0.00 | 37 761.99 | 0.01 |
| 71.7-61.6 | 37 322.02 | -0.01 | 37 428.52 | 0.00 | 37 529.66 | 0.00 | 37 627.14 | 0.01 |
| 71.6-71.7 | 26 972.64 | -0.01 | 26 874.27 | 0.00 | 26 781.16 | -0.01 | | |
| 81.7-81.8 | 32 289.64 | 0.01 | | _ | 32 037.86 | 0.02 | 31 919.79 | -0.02 |
| 91.8-91.0 | | | | | | _ | 36 919.96 | 0.01 |
| 92.7-92.8 | 26 845.74 | 0.01 | 26 790.78 | 0.00 | 26 740.61 | 0.01 | 26 694.03 | 0.00 |
| 02.8-102.9 | 32 943,55 | -0.02 | 32 853.00 | 0.02 | 32 768.45 | 0.06 | | |
| 12.9-112.10 | 38 736.92 | 0.00 | 38 607.73 | 0.01 | 38 485.72 | -0.01 | 38 368.90 | -0.01 |
| 23.9-123.10 | 31 616.71 | -0.02 | 31 591.91 | 0.01 | 31 572.22 | 0.00 | 31 556.41 | 0.01 |
| 133,10-133,11 | 38 345.44 | -0.02 | 38 277.22 | -0.01 | 38 215.27 | 0.00 | 38 157.91 | 0.01 |
| 144.10-144.11 | | | | | | | — | |
| 154,11-154,12 | | | - | | 35 945.51 | 0.01 | 35 974.53 | 0.01 |
| 175,12-175,13 | | | | | 31 781.42 | 0.00 | 31 907.16 | 0.00 |
| 72,6-70,7 | 29 446.32 | 0.00 | 29 301.44 | 0.01 | 29 162.87 | 0.01 | 29 028.92 | 0.01 |
| 82.7-80.8 | 33 636.86 | 0.01 | 33 478.15 | 0.00 | | | _ | |
| 83,6-81,7 | 30 930.29 | 0.00 | 30 740.29 | 0.01 | 30 557.55 | 0.01 | | |
| 93,7-91,8 | | | — | | — | | 33 105.61 | -0.02 |
| 103,8-101,9 | 37 099.58 | 0.01 | 36 917.31 | -0.01 | | | 36 575.16 | 0.01 |
| 104,7-102,8 | 38 211.35 | 0.01 | 37 922.21 | 0.00 | | | 37 371.12 | 0.01 |
| 14.8-112.0 | 39 163.00 | 0.01 | 38 906.24 | 0.00 | 38 659.36 | 0.00 | 38 419.82 | -0.01 |

TABLE 1.—ASSIGNED ROTATIONAL TRANSITIONS FOR THE GROUND STATE,

and 3 g of anhydrous Na_2CO_3 in an autoclave at 160-170°C for 24 h.²¹ Dicyclopentadiene extracted from the residue with ether and purified by vacuum distillation, was then converted to cyclopent-3-enone as above. The microwave spectrum of the resulting sample indicated that the [2-D] and [3-D] compounds were in the ratio 2 :1, as expected.

SPECTRA

The spectra of the parent and synthetically prepared isotopic varieties of cyclopent-3enone were observed at room temperature using a Hewlett-Packard 8460 A R-band spectrometer with Stark modulation at 33.33 kHz. The spectra of the [¹³C] species in natural abundance were recorded at about -40° C to enhance their intensity. Precision of frequency measurement is estimated as 0.03 MHz for the common, [¹⁸O] and [2-D] species and 0.07 MHz for all others.

RESULTS

GROUND STATE SPECTRUM

Cyclopent-3-enone is a near-prolate asymmetric rotor ($\kappa = -0.544$) with the dipole moment restricted by symmetry to lie along the *a*-axis. The rotational spectrum is therefore dominated by strong μ_a , R-branch transitions which can be straightforwardly assigned through their characteristic Stark effect patterns. Initial rotational constants were obtained from a rigid rotor, least squares analysis of the low *J*, R-branch transitions. Final constants were determined using a Watson first order centrifugal distortion analysis ²² of data which included higher *J*, Q-branch transitions in order to determine better the constant *A*. Observed frequencies and

$V_{\rm B} = 1$ to $V_{\rm B} = 7$ states, and $V_{\rm T} = 1$ state of cyclopent-3-enone

| | obs. | | obs. | | obs. | | obs. | | obs |
|-------------|--------|---------------|--------|---------------|--------|---------------|--------|---------------|---------|
| obs. | -calc. | obs. | -calc. | obs. | -calc. | obs. | -calc. | obs. | - calc. |
| $V_{\rm B}$ | = 4 | $V_{\rm B} =$ | = 5 | $V_{\rm B} =$ | = 6 | $V_{\rm B} =$ | - 7 | $V_{\rm T} =$ | - 1 |
| 27 894.41 | 0.00 | 27 954.44 | -0.01 | 28 008.99 | -0.06 | 28 071.56 | -0.01 | | |
| 27 397.01 | -0.01 | 27 462.96 | -0.01 | | | | | — | |
| 32 390.61 | -0.02 | 32 441.90 | -0.10 | 32 488.82 | 0.10 | | _ | 32 159.52 | 0.07 |
| 33 323.82 | -0.01 | 33 386.05 | 0.00 | 33 443.31 | 0.12 | 33 508.91 | 0.06 | 33 039,32 | 0.10 |
| 30 382.37 | 0.00 | 30 442.86 | 0.01 | 30 498.19 | 0.09 | 30 561.49 | 0.03 | 30 115.69 | 0.08 |
| 31 874.13 | -0.02 | 31 940.94 | 0.00 | 32 002.34 | -0.07 | 32 072.85 | 0.00 | 31 573.92 | 0.05 |
| 31 358.92 | 0.02 | 31 421.66 | 0.05 | 31 479.06 | -0.06 | 31 545.05 | 0.00 | | |
| 32 857.85 | 0.06 | 32 932.87 | 0.04 | 33 001.24 | 0.03 | 33 079.36 | 0.03 | 32 538.45 | 0.00 |
| 37 967.06 | -0.02 | 38 025.53 | 0.04 | 38 078.36 | -0.13 | 38 139.65 | -0.03 | 37 707.62 | -0.05 |
| 32 587.76 | -0.00 | 32 666.97 | -0.01 | 32 739.27 | 0.01 | 32 821.65 | -0.02 | 32 249.42 | 0.01 |
| 36 088.29 | 0.01 | 36 159.85 | 0.01 | 36 225.24 | 0.04 | 36 300.08 | -0.01 | 35 774.08 | -0.03 |
| | | | | | | _ | _ | 39 845.78 | -0.05 |
| 38 848.84 | 0.00 | 38 931.15 | 0.03 | 39 007.00 | -0.07 | 39 093.89 | -0.05 | 38 476.56 | -0.07 |
| 37 619.81 | 0.00 | 37 693.93 | 0.00 | | | | | 37 288.82 | -0.07 |
| | | 37 901.44 | -0.11 | | | | | | |
| _ | | 37 806.03 | 0.09 | | | | | | |
| 37 854.33 | 0.00 | 37 944.69 | 0.00 | | | | | | |
| 37 721.96 | -0.02 | 37 814.80 | -0.03 | | | | | 37,326.27 | 0.00 |
| 26 605.55 | 0.00 | 26 521.68 | -0.03 | | | | | | |
| | _ | | | | | | | | |
| 36 778.59 | 0.04 | 36 640.65 | 0.05 | | | | | | |
| 26 650.26 | 0.01 | 26 608.70 | 0.03 | | | | | | |
| 32 611.31 | 0.05 | | | | | | | | |
| 38 256.18 | 0.04 | 38 146.61 | 0.05 | | | | | | |
| | | _ | | | | | | | |
| 38 104.02 | -0.02 | | _ | | | | | | |
| 28 607.60 | 0.01 | 28 676.37 | 0.01 | | | | | | |
| 36 006.59 | 0.02 | | | | | | | | |
| 32.036.07 | -0.01 | | | | | | | | |
| | | _ | | | | | | | |
| | | | _ | | | | | | |
| | | 30 037.86 | 0.05 | | | | | | |
| 32 941.26 | 0.00 | | | | | | | | |
| 36 411.87 | 0.00 | | | | | | | | |
| 37 105.12 | -0.01 | 36 844.19 | -0.03 | | | | | | |
| 38 186.26 | 0.01 | _ | | | | | | | |

their difference from those calculated from the Watson treatment are recorded in table 1. Rotational constants, moments of inertia and the quantity $\Delta_0 = I_c^\circ - I_a^\circ - I_b^\circ$ are given in table 2. The centrifugal distortion constants were not well determined because of an insufficient number of subbranches and therefore are not recorded here. However, there is evidence that the rotational constants so determined are better than could be obtained through a rigid rotor treatment.²³

TABLE 2.—ROTATIONAL CONSTANTS ^{*a*} AND MOMENTS OF INERTIA ^{*b*} FOR THE GROUND STATE, $V_{\rm B} = 1$ to $V_{\rm B} = 7$ states and the $V_{\rm T} = 1$ state of cyclopent-3-enone

| A | В | С | Ia | Ib | Ie | Δ_V |
|---------|---|---|---|---|--|---|
| 7378.33 | 3615.209 | 2503.587 | 68.4947 | 139.7917 | 201.8607 | -6.4257 |
| 7352.03 | 3620.805 | 2511.911 | 68.7397 | 139.5756 | 201.1918 | -7.1235 |
| 7326.42 | 3626.199 | 2519.813 | 68.9800 | 139.3680 | 200.5609 | -7.7871 |
| 7301.33 | 3631.476 | 2527.432 | 69.2169 | 139.1654 | 199.9563 | -8.4260 |
| 7276.69 | 3636.685 | 2534.846 | 69.4514 | 138.9661 | 199.3715 | -9.0460 |
| 7252.39 | 3641.845 | 2542.103 | 69.6840 | 138.7692 | 198.8024 | -9.6508 |
| 7229.54 | 3646.553 | 2548.719 | 69.904 | 138,590 | 198.286 | -10,208 |
| 7204.72 | 3652.055 | 2556.249 | 70.145 | 138.381 | 197.702 | -10.824 |
| 7379.54 | 3612,222 | 2504.172 | 68.483 | 139.907 | 201.814 | -6.576 |
| | A 7378.33 7352.03 7326.42 7301.33 7276.69 7252.39 7229.54 7229.54 7204.72 7379.54 | A B 7378.33 3615.209 7352.03 3620.805 7326.42 3626.199 7301.33 3631.476 7276.69 3636.685 7229.54 3644.845 7229.54 3646.553 7204.72 3652.055 7379.54 3612.222 | A B C 7378.33 3615.209 2503.587 7352.03 3620.805 2511.911 7326.42 3626.199 2519.813 7301.33 3631.476 2527.432 7276.69 3636.685 2534.846 7229.54 3646.553 2542.103 7204.72 3652.055 2556.249 7379.54 3612.222 2504.172 | $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ | $ \begin{array}{c ccccccccccccccccccccccccccccccccccc$ | $ \begin{array}{c c c c c c c c c c c c c c c c c c c $ |

^a Rotational constants are in MHz and moments of inertia in a.m.u. Å². The estimated uncertainties are ± 0.01 MHz for A, ± 0.001 MHz for B and C up to $V_B = 5$. For $V_B > 5$ and $V_T = 1$, the uncertainties are ± 0.2 MHz for A and ± 0.005 MHz for B and C. ^b Conversion factor is BI = 505 376 (MHz) (a.m.u. Å²).

VIBRATIONAL SATELLITES

An extended vibrational satellite series, with several members observable, accompanies each R branch transition to high frequency and is readily assigned to successive quanta of the ring bending vibration (v_B) . Observed frequencies for rotational transitions in states of v_B with vibrational quantum number $V_B = 1$ through to $V_B = 7$ are also recorded in table 1 while the corresponding rotational constants, moments of inertia and Δ_V are included in table 2. A detailed discussion of the use of this satellite series in the determination of a potential energy function for the ring bending vibration is given in Part 2.¹⁷

The effect of nuclear spin statistics on intensities within the ring bending satellite series is clearly seen for the $5_{3,2}-4_{3,1}$ transition in fig. 2. There is conclusive evidence from both the microwave and far infra-red spectra that cyclopent-3-enone has a planar equilibrium ring structure and C_{2v} symmetry, with the *a*-axis as the symmetry axis. Consequently, a twofold rotation about a exchanges three pairs of equivalent protons of spin $I = \frac{1}{2}$ and therefore the total molecular wavefunction must be antisymmetric with respect to this operation. However, the vibrational wavefunction is symmetric for even values of $V_{\rm B}$ since the ring bending mode (B_1) is itself antisymmetric with respect to C_2^a . Thus, the rotational states (ee, eo), symmetric with respect to this operation, must be combined with the 7 antisymmetric nuclear spin functions when $V_{\rm B}$ is even but with the 9 symmetric spin functions when $V_{\rm B}$ is odd. For the antisymmetric rotational states (oo, oe) the reverse is true. Only when these nuclear spin statistical weight factors are properly taken into account do relative intensity measurements among, for example, the satellites shown in fig. 2 give rise to the smoothly increasing vibrational separations demanded both by the smooth variation of the rotational constants with $V_{\rm B}$ and the far infra-red spectrum.¹⁷

Another vibrational satellite, associated with the first excited state of the ring twisting mode (v_T) , has also been assigned. Observed frequencies are recorded in table 1 and rotational constants in table 2. It should be noted that for the states $V_T = 1$ and $V_B = 6$ to 7 the number of transitions available were sufficient only for a

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rigid rotor treatment. The ring twisting mode (A_2) is symmetric with respect to C_2 and hence the statistical weight ratio for the ground vibrational state to the $V_T = 1$ satellite for a given rotational transition is unity. A quantitative discussion of this vibration is given in Part 2.¹⁷



FIG. 2.—Ring bending vibrational satellite series (V_B) of the $5_{3,2}-4_{3,1}$ transition of cyclopent-3-enone showing the effects of nuclear spin statistics.

MOLECULAR PLANARITY

The coplanarity of the heavy atoms of cyclopent-3-enone is conclusively established from several aspects of its microwave spectrum and from its far infra-red spectrum.

The first argument involves the quantities $\Delta_V = I_c^V - I_a^V - I_b^V$ (see table 2). In the vibrational ground state the only contribution to Δ_0 is from the out-of-plane (c_H) coordinates of the methylenic hydrogen atoms according to the equation

$$\Delta_0 = -8m_{\rm H}c_{\rm H}^2$$

if the inertia defect is neglected and the molecule is planar. The value $-6.39 \text{ a.m.u.} \text{Å}^2$ so calculated from the reasonable methylene group parameters r(C-H) = 1.09 Åand $\angle HCH = 109^{\circ} 28'$ agrees well with the experimental value and strongly suggests that only the methylenic hydrogen atoms are out of the molecular plane. Also consistent with this conclusion are the essentially identical values of the corresponding quantity for the isotopic species where substitution is in the plane of the ring (table 5). Moreover, the progressively more negative value of Δ_{V} as the vibrational quantum numbers associated with the ring bending and twisting modes increase indicates that each of these motions takes atoms away from the plane.

A very high barrier to the planar structure in cyclopent-3-enone, involving other than methylenic hydrogen atoms out-of-plane, is thus ruled out by the moments of inertia. An intermediate barrier is also excluded by the rigid rotor behaviour of the spectrum and the absence of detectable line doubling in any vibrational state. However, a very low barrier to the planar ring in the potential energy function, lower than

even the zero point vibrational level, as in cyclobutanone ³ and trimethylene oxide,¹ is not inconsistent with the value of Δ_0 . A second and more sensitive test of a strictly planar equilibrium ring structure is the smooth variation of the rotational constant differences $A_V - A_0$, etc., as a function of the ring bending quantum number V_B shown in fig. 3. If the equilibrium ring structure were even very slightly non-planar, corresponding to a double minimum potential function for the bending vibration with a very low barrier, the curves in fig. 3 would show a significant zig-zag effect between $V_B = 0$, 1 and 2 due to the differential perturbation of these states by the barrier.¹ Evidence on similar lines comes from the smooth variation of the v_B vibrational separations as determined from the far infra-red spectrum ¹⁷ (see Part 2).



FIG. 3.—Variation of rotational constants as a function of the ring bending vibrational quantum number, $V_{\rm B}$.

SPECTRA OF ISOTOPIC SPECIES

The $[^{13}C]$ isotopic species of cyclopent-3-enone have been assigned in their natural abundances of 1.2, 2.3 and 2.3 % for single substitution at the 1, 2 and 3 positions respectively. As a rough indication of the region to be searched for a particular species, the changes in moments of inertia on isotopic substitution were calculated from a model structure and added to the observed moments of inertia of the common species to give an approximation to the required rotational constants.

Initial assignments were greatly facilitated by sweeps at very low Stark electric field strengths (~8 V cm⁻¹) of the regions of interest. Even for quite asymmetric prolate rotors the splitting between the components of the high K_{-1} doublet levels of a given J, for example ($5_{5,1}, 5_{5,0}$) or ($6_{5,1}, 6_{5,2}$), is very small. Consequent upon these near-degeneracies, the two allowed μ_a , R-branch transitions ($6_{5,2}-5_{5,1}$) and ($6_{5,1}-5_{5,0}$), have very fast Stark effects. Moreover, the Stark effect of one moves to high frequency with increasing field while the other moves to low frequency. Thus at very low electric field strengths, when little else is modulated, this pair of nearly coincident

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transitions stands out as a broad line with a symmetrical Stark effect. Fig. 4 shows a trace of this feature for the parent and $[3^{-13}C]$ species. The difference in attenuation between the two traces is that required for 2 % abundance of the $[^{13}C]$ species.



FIG. 4.—Unresolved $6_{5,1}-5_{5,0}$ and $6_{5,2}-5_{5,1}$ transitions in parent (a) and $[3^{-13}C]$ cyclopent-3-enone (b) at a Stark field of approximately 8 V cm⁻¹.

Further assignments were made on the basis of correct Stark effect patterns and correct relative intensities. Observed frequencies for the limited number of transitions available and their difference from those calculated in a rigid rotor least squares analysis are shown in table 3 while rotational constants and moments of inertia are

Table 3.—Assigned rotational transitions of the $[^{13}C]$ cyclopent-3-enones and [3-D]cyclopent-3-enone in the vibrational ground state

| | [1-130 | C] | [2-13 | C] | [3-1 | 3C] | [3- | D] |
|-------------------|-----------|----------|-----------|----------|-----------|----------|-----------|----------|
| transition | obs. | obscalc. | obs. | obscalc. | obs. | obscale. | obs. | obscale. |
| 50,5-40,4 | | _ | | | 27 290.63 | -0.01 | | |
| 51,5-41,4 | 27 024.56 | 0.05 | | | 26 760.49 | 0.05 | | |
| $5_{1,4}-4_{1,3}$ | | | 32 024.61 | 0.00 | | | | |
| 52,3-42,2 | 32 912.56 | 0.09 | 33 057.37 | 0.05 | 32 554.27 | 0.06 | 31 765.60 | 0.03 |
| 52,4-42,3 | 30 011.70 | 0.06 | | - | 29 706.66 | 0.04 | | |
| 53.2-43.1 | | | 31 582.08 | 0.01 | - | | _ | — |
| 53,3-43,2 | 30 965.36 | 0.06 | 31 022.79 | 0.09 | 30 639.89 | -0.02 | | |
| 60,6-50,5 | 32 435.81 | -0.14 | 32 275.66 | 0.02 | 32 127.15 | -0.01 | 31 429.80 | 0.03 |
| $6_{1,6}-5_{1,5}$ | 32 143.36 | 0.04 | 32 019.89 | 0.03 | 31 831.20 | -0.03 | 31 128.81 | 0.04 |
| 61,5-51,4 | | | | | | | 36 397.90 | 0.03 |
| 62,5-52,4 | 35 653.17 | 0.01 | 35 605.10 | -0.02 | 35 295.19 | 0.04 | 34 494.91 | 0.01 |
| 62,4-52,3 | 39 698.44 | 0.07 | 39 821.93 | -0.04 | 39 274.03 | -0.02 | 38 336.42 | 0.02 |
| 63,3-53,2 | 38 323.44 | -0.08 | 38 533.36 | -0.06 | | | 36 972.36 | 0.00 |
| 63,4-53,3 | | — | | | 36 765.64 | -0.08 | 35 904.27 | -0.05 |
| 70,7-60,6 | 37 350.39 | 0.01 | 37 133.97 | 0.04 | — | — | 36 187.09 | -0.01 |
| 71,7-61,6 | 37 204.05 | 0.00 | - | | | | | |
| 72,6-62,5 | | | | - | | _ | 39 811.12 | -0.06 |

recorded in table 5. The rigid rotor treatment is justified by the small contributions from centrifugal distortion to the frequencies recorded in table 3, generally less than 0.3 MHz. When the transitions were corrected for the centrifugal distortion contributions pertinent to the corresponding transitions of the parent species and a rigid rotor analysis then executed, the rotational constants agreed with those of table 5 within the error quoted.

The possibility that one or more of the rigid rotor transition sets shown in table 3

belongs not to a [13C] species but to some vibrational satellite can be excluded for several reasons. First, relative intensities are in agreement with expected natural abundances and are invariant between 25 and -40° C. Second, for the [1-13C] species both the rotational constant A and the nuclear spin statistical weight effects are essentially unchanged from the common species, indicating the substituted atom to be on the symmetry axis. On the other hand, for the [2-13C] and [3-13C] molecules the statistical weight effects vanish and A changes. Third, Δ_0 is essentially identical for the three [13C] species and the common species (tables 2 and 5) whereas for the out-of-plane vibrations, v_T and v_B , Δ_V becomes more negative. For in-plane vibrations

| TABLE | 4.—Assigned | ROTATIONAL | TRANSITIONS | OF [¹⁸ O]- | AND | [2-D]-CYCLOPENT-3-ENONE |
|-------|-------------|------------|-------------|------------------------|------|-------------------------|
| | | IN THE | VIBRATIONAL | GROUND ST | TATE | |

| | t1 | ⁸ O1 | [2-D | |
|--|-------------------|-----------------|-------------------|----------|
| transition | obs, | obscalc. | obs. | obscalc. |
| $5_{0,5} - 4_{0,4}$ | 26 629.76 | 0.03 | | <u> </u> |
| $5_{1,5}-4_{1,4}$ | | | 26 669.89 | -0.00 |
| $5_{1,4}-4_{1,3}$ | 30 740.70 | -0.06 | 31 715.59 | -0.04 |
| $5_{2,3}-4_{2,2}$ | 31 285.45 | 0.00 | 32 911.05 | -0.00 |
| $5_{2,4} - 4_{2,3}$ | | | 29 749.33 | 0.02 |
| 5 _{3,2} -4 _{3,1} | 29 934.10 | -0.06 | 31 463.45 | -0.03 |
| $5_{3,3}$ - $4_{3,2}$ | 29 573.50 | 0.11 | 30 832.53 | 0.02 |
| 6 _{0,6} -5 _{0,5} | 31 347.90 | 0.09 | 31 914.81 | 0.02 |
| 6 _{1,6} –5 _{1,5} | 30 995.66 | 0.01 | 31 698.52 | 0.01 |
| $6_{1,5}-5_{1,4}$ | 36 181.68 | -0.10 | 37 038.56 | 0.01 |
| 62,5-52,4 | 34 230.79 | 0.01 | 35 284.87 | 0.01 |
| $6_{2,4}-5_{2,3}$ | 37 810.27 | -0.01 | 39 585.47 | 0.00 |
| 63,3-53,2 | 36 389.51 | -0.03 | 38 433.16 | 0.01 |
| $6_{3,4}-5_{3,3}$ | 35 502.87 | 0.01 | | |
| 70,7-60,6 | 36 082.59 | 0.01 | 36 773.60 | 0.00 |
| $7_{1,7}-6_{1,6}$ | 35 893.63 | 0.01 | 36 673.95 | -0.02 |
| $7_{2,6}-6_{2,5}$ | 39 547.59 | -0.02 | | |
| 81,7-81,8 | 30 462.97 | -0.01 | 31 822.52 | 0.03 |
| 9 _{1,8} -9 _{1,9} | | | 36 650.58 | 0.04 |
| 10 _{2,8} –10 _{2,9} | 30 056.85 | -0.02 | 33 294.79 | 0.00 |
| 11 _{2,9} -11 _{2,10} | 35 868.57 | 0.00 | 38 671.00 | -0.01 |
| 11 _{3,8} -11 _{3,9} | | | 26 691.84 | 0.00 |
| $12_{3,9} - 12_{3,10}$ | | | 33 256.23 | 0.00 |
| 14 _{4,10} 14 _{4,11} | | | 31 560.85 | 0.00 |
| $15_{4,11}$ - $15_{4,12}$ | 29 930.33 | 0.01 | | |
| 164,12-164,13 | 37 240.85 | 0.00 | | |
| $17_{5,12} - 17_{5,13}$ | | | 36 269.99 | 0.00 |
| $18_{5,13} - 18_{5,14}$ | 31 796.3 6 | 0.00 | | |
| 19 _{6,13} –19 _{6,14} | | | 32 278.36 | 0.09 |
| 82,7-80,8 | | | 32 691.76 | -0.03 |
| 9 _{2,8} -9 _{1,9} | 36 545,99 | 0.00 | | |
| 8 _{3,6} -8 _{1,7} | | | 29 215.12 | 0.00 |
| 9 _{3,7} -9 _{1,8} | 33 053.32 | 0.02 | 32 263.81 | 0.00 |
| 10 _{3,8} –10 _{1,9} | 35 9 77.83 | -0.01 | 35 958.4 3 | 0.01 |
| 11 _{3,9} –11 _{1,10} | 39 515.89 | 0.00 | | |
| 84,5-82,6 | _ | | 35 512.65 | -0.15 |
| 9 _{4,6} -9 _{2,7} | | | 34 625.00 | -0.10 |
| 10 _{4,7} -10 _{2,8} | | | 35 035.34 | -0.06 |
| 11 _{4,8} –11 _{2,9} | 39 715.03 | -0.01 | | |

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 Δ_V is expected to become less negative.²⁴ A fourth compelling argument in favour of the assignment is that the $V_{\rm B} = 1$ satellites for the [2-¹³C] and [3-¹³C] species have been assigned (that associated with the 1-position was obscured by common species transitions) and the $\Delta_1 = -7.129$ and -7.128 a.m.u.Å² respectively are essentially identical to the common species value -7.124 a.m.u.Å².

TABLE 5.—ROTATIONAL CONSTANTS ^{*a*} AND MOMENTS OF INERTIA FOR THE VIBRATIONAL GROUND STATE OF THE ISOTOPICALLY SUBSTITUTED SPECIES OF CYCLOPENT-3-ENONE

| isotope | A | В | С | I_a | Ib | Ic | Δ_0 |
|---------|---------|----------|----------|---------|----------|----------|------------|
| [1-13C] | 7378.68 | 3598.79 | 2495.77 | 68.4914 | 140.429 | 202.493 | -6.427 |
| [2-13C] | 7217.16 | 3615.07 | 2484.67 | 70.0243 | 139,797 | 203.398 | -6.423 |
| [3-13C] | 7332.10 | 3559.75 | 2471.66 | 68.9265 | 141.969 | 204.468 | 6.428 |
| 11801 | 7378.18 | 3421.510 | 2409.136 | 68,4960 | 147,7056 | 209.7748 | -6.4268 |
| [2-D] | 6951.27 | 3596.396 | 2460.956 | 72.7027 | 140.5229 | 205.3576 | 7.8680 |
| [3-D] | 7217.99 | 3473.83 | 2417.32 | 70.0162 | 145.481 | 209.064 | -6.433 |

^a Rotational constants are in MHz and moments of inertia are in a.m.u. Å². Estimated uncertainties are ± 0.01 MHz in A and ± 0.001 MHz in B and C for [1^a0] and [2-D]. For the remaining species, estimated uncertainties are 0.2, 0.01, and 0.01 MHz for A, B, and C respectively.

The spectra of [¹⁸O] and [2-D]cyclopent-3-enone were easily assigned because substantial isotopic enrichment was possible. The method of preparation of the [3-D] species allowed only low enrichment (~3 %) but ensured a statistical distribution of [2-D] and [3-D] compounds. Thus, the previously assigned spectrum of [2-D] was first identified and then the [3-D] species spectrum with half the intensity sought. Frequencies of the transitions of the [¹⁸O] and [2-D] isotopic varieties are displayed in table 4 while those of the [3-D] species are included in table 3. Spectral constants, from a centrifugal distortion analysis for [¹⁸O] and [2-D] and a rigid rotor analysis for [3-D], are in table 5. We note that the [¹⁸O] species (like 1-[¹³C]) has A, Δ_0 and nuclear spin statistics unchanged from the common species.

MOLECULAR GEOMETRY

Accurate ground state effective moments of inertia are available for the six different singly substituted isotopic varieties of cyclopent-3-enone as well as the parent compound. The r_s -coordinates of each atom referred to the principal inertial axis system of the parent molecule can therefore be determined from Kraitchman's equations ^{25, 26} for a non-planar asymmetric rotor:

$$\alpha^{2} = \frac{\Delta P_{\alpha}}{\mu} \left(1 + \frac{\Delta P_{\beta}}{I_{\alpha} - I_{\beta}} \right) \left(1 + \frac{\Delta P_{\gamma}}{I_{\alpha} - I_{\beta}} \right)$$

where α , β , and γ are cyclically permuted among *a*, *b*, and *c* and

$$\Delta P_{\alpha} = \frac{1}{2}(-\Delta I_{\alpha} + \Delta I_{\beta} + \Delta I_{\gamma})$$

$$\Delta P_{\beta} = \frac{1}{2}(-\Delta I_{\beta} + \Delta I_{\gamma} + \Delta I_{\alpha})$$

$$\Delta P_{\gamma} = \frac{1}{2}(-\Delta I_{\gamma} + \Delta I_{\alpha} + \Delta I_{\beta}).$$

Here, $\mu = \Delta m M / (\Delta m + M)$ and ΔI and ΔM are respectively the changes in the moments of inertia, *I*, and the mass, *M*, of the parent molecule on isotopic substitution. The r_s -coordinates so calculated are given in table 6. The only possible ambiguities in the signs of the coordinates were for $a(C_2)$ and $a(H_2)$, both of which are small. However, the negative sign for $a(C_2)$ must be chosen, for otherwise $r(C_1-C_2) = 1.438$ Å and $r(C_2-C_3) = 1.658$ Å, which values are respectively unreasonably short and long for a sp^2-sp^3 , C—C bond. Similarly only when the positive value of $a(H_2)$

is chosen does the expected small angle (0° 15') between the projection of the C_2 —H₂ bond on the *ab* plane and the bisector of $\angle C_1C_2C_3$ result, otherwise the unreasonably large value 17° 48' is obtained.

TABLE 6.— r_s -coordinates * of cyclopent-3-enone in the principal axis system (Å)

| | | principal axis coordinates | |
|--------|----------------------|----------------------------|-------------------------|
| atom † | a | ь | с |
| 0 | 2.0111 ± 0.0006 | 0 | 0 |
| C_1 | 0.8015 ± 0.0019 | 0 | 0 |
| C_2 | $- 0.079 \pm 0.019$ | $\pm 1.2427 \pm 0.0012$ | 0 |
| C_3 | -1.4773 ± 0.0010 | $\pm 0.6692 \pm 0.0023$ | 0 |
| H_2 | 0.0977±0.0012 | $\pm 1.8613 \pm 0.0001$ | $\pm 0.8750 \pm 0.0001$ |
| H_3 | -2.3648 ± 0.0012 | $\pm 1.2835 \pm 0.0007$ | 0 |

* The errors quoted follow from those obtained for the rotational constant in the least squares analysis. † The numbering scheme for the atoms is indicated in fig. 1.

The coordinates of table 6 lead to the r_s -structure given in column I of table 7. Unfortunately, two of the coordinates are smaller than the lower limit of 0.15 Å set by Costain ²⁶ for reliably determined r_s -coordinates and are assumed to be underestimated. An alternative procedure for $a(C_2)$ and $a(H_2)$ is to use the r_s -coordinates of all other atoms in the first and second moment equations $\sum_i m_i a_i = 0$ and $I_b = \sum_i m_i (a_i^2 + c_i^2)$. However, as discussed by Costain,²⁶ this procedure requires that the whole difference $I^\circ - I^s$ must be taken up in the two small coordinates to be determined and is here clearly unsatisfactory.

TABLE 7.—MOLECULAR STRUCTURES ^a OF CYCLOPENT-3-ENONE

| parameter | I | II | III |
|-------------------------|----------|---------------------------------|----------|
| r(C==0) | 1.210 | 1.210 ± 0.002 | 1.210 |
| $r(C_1 - C_2)$ | 1.523 | 1.524 ± 0.008 | 1.526 |
| $r(C_2 - C_3)$ | 1.511 | 1.509±0.008 | 1.506 |
| $r(C_3 - C_{3'})$ | 1.338 | 1.338 <u>+</u> 0.004 | 1.338 |
| $r(C_2 - H_2)$ | 1.086 | 1.086 ± 0.004 | (1.090) |
| $r(C_3 - H_3)$ | 1.079 | 1.079 ± 0.003 | 1.079 |
| $\angle C_2 C_1 C_{2'}$ | 109° 20' | $109^{\circ} 12' \pm 1^{\circ}$ | 109° 04′ |
| $\angle C_1 C_2 C_3$ | 103° 02′ | $103^{\circ} 08' \pm 48'$ | 103° 05′ |
| $\angle C_2 C_3 C_{3'}$ | 112° 18′ | $112^{\circ} 26' \pm 18'$ | 112° 23′ |
| $\angle H_2C_2H_2$ | 107° 18′ | $107^{\circ} 18' \pm 40'$ | 106° 58′ |
| $\angle H_3C_3C_2$ | 124° 42′ | $124^{\circ} 42' \pm 16'$ | 124° 42′ |
| θ^{b} | 0° 15′ | 0° 00′ | - 2° 01′ |
| | | | |

^{*a*} Column I is the complete r_s -structure. Column II uses $a(C_2) = -0.0816$ Å as calculated from $\Sigma_i m_i a_i = 0$. Column III uses $a(C_2)$ and $a(H_2)$ calculated from $\Sigma_i m_i a_i = 0$ assuming r(C-H) = 1.090 Å (see text). ^{*b*} θ is the angle between the projection of C_2 —H₂ on the *ab* plane and the bisector of $\angle C_1 C_2 C_3$.

In the present situation, $a(C_2)$ is critically involved in the determination of the ring structure and must be obtained as accurately as possible whereas $a(H_2)$ is of peripheral interest only. We note that the contribution of $a(H_2)$ to the first moment equation $\sum_i m_i a_i = 0$ is quite small, about one sixth of that of $a(C_2)$. Thus a reasonable procedure is to use the value of $a(H_2)$ from Kraitchman's equation with all other r_s , *a*-coordinates in the first moment equation to determine $a(C_2)$. The smallness of contribution of the hydrogen atom to $\sum_i m_i a_i = 0$ will ensure that any small error in

its r_s -coordinate will not seriously affect the determination of $a(C_2)$. Table 8 shows that the value of $a(C_2)$ so calculated is in good agreement with but slightly larger than the r_s -value. The structure which results when this value of $a(C_2)$ is used with r_s coordinates of the atoms is in column II of table 7.

| TABLE 8.—Small coordinates in cyclopent-3-enone | | | | | |
|---|----------------------|------------------------------|--|--|--|
| method of determination | a(C ₂)/Å | <i>a</i> (H ₂)/Å | | | |
| Kraitchman's equation $\Sigma_i m_i a_i$ to give $a(C_2)$ | -0.0795 -0.0816 | +0.0977 | | | |
| $\Sigma_i m_i a_i$ using r(CH) = 1.090±0.005 Å | -0.0845 ± 0.005 | $+0.115\pm0.02$ | | | |

The reliability of $a(C_2)$ can be further tested. If $r(C_2 - H_2)$ is assumed as 1.090 ± 0.005 Å, which is a reasonable estimate for a methylenic C—H bond, the r_s -coordinates $b(C_2)$, $b(H_2)$ and $c(H_2)$ can be used to give the relationship $a(C_2) = -0.1997 +$ $a(H_2)$. Both small a-coordinates can then be determined from the first moment equation. Table 8 shows that while $a(H_2)$ so determined is very sensitive to small changes in $r(C_2-H_2)$, $a(C_2)$ is much less so and its value is in excellent agreement with that calculated by the other methods. The structure which results when $r(C_2 - H_2)$ is assumed is given in column III of table 7. The errors reported for the structure in table 7, column II are those transmitted from the uncertainties in the rotational constants via the r_s -coordinates with an assumed error of ± 0.005 Å in $a(C_2)$. The best $r_{\rm s}$ -structure for cyclopent-3-enone is taken to be that in column II and is shown in fig. 1.

DIPOLE MOMENT

The dipole moment of cyclopent-3-enone, restricted by symmetry to lie along the a-axis, was measured using the Stark shift of various M components of the $5_{2,4}-4_{2,3}$, $5_{1,5}-4_{1,4}$ and $6_{0,6}-5_{0,5}$ transitions in the vibrational ground state of the common

| transition | M _J component | $(\Delta \nu / E^2 \times 10^5) / (V^{-2} \text{ cm}^2 \text{ MHz})$ | dipole moment (μ/D) |
|---------------------|--------------------------|--|-------------------------|
| $5_{2,4}-4_{2,3}$ | 1 | 0.514 ₅ | $2.79_3 \pm 0.01_6$ |
| | 2 | 2.062 | $2.79_0 \pm 0.01_6$ |
| | 3 | 4.63 ₀ | $2.78_7 \pm 0.02_1$ |
| $5_{1.5} - 4_{1.4}$ | 2 | 0.1466 | $2.76_2 \pm 0.01_8$ |
| | 3 | 0.4871 | $2.80_4 \pm 0.01_4$ |
| | 4 | 0.979 ₃ | $2.83_5 \pm 0.03_2$ |
| $6_{0.6} - 5_{0.5}$ | 4 | 0.195 ₂ | $2.75_{5} \pm 0.01_{8}$ |
| , -,- | 5 | 0.3595 | $2.82_8 \pm 0.02_1$ |

| Table 9.—Dipole | MOMENT | OF • | CYCLOPENT- | 3-ENONE |
|-----------------|--------|------|------------|---------|
|-----------------|--------|------|------------|---------|

species. For each of these transitions the Stark shifts of the components, Δv , were found to be strictly proportional to the square of the applied electric field, E^2 . The Stark cell was calibrated using the $J = 2 \leftarrow 1$, K = 0 transition in the vibrational ground state of ¹²CH₃¹²C \equiv ¹²CH, for which $\mu = 0.7840$ D.²⁷ The values of $\Delta v/E^2$ (MHz V⁻² cm²) and μ (D) for cyclopent-3-enone are displayed in table 9. The mean value is $\mu = 2.79 \pm 0.02_8$.

DISCUSSION

A planar equilibrium ring structure has been established for cyclopent-3-enone. This configuration is to be expected from the minimum ring angle strain and the staggered C—H bonds between C_2 and C_3 which then result. The only unfavourable factor is the staggering of the C=O and adjacent methylenic C-H bonds consequent upon the planar ring. In molecules where a methyl group is attached to a carbonyl group and is free to rotate to the energetically most favourable position, for example acetaldehyde, one C—H bond of the methyl group eclipses the C=O bond 28 and the methyl group is tilted towards the oxygen atom.²⁹

The bond lengths of cyclopent-3-enone agree closely with the r_s -distances for the corresponding bond type in open chain and ring systems. Thus, the sp^3 - sp^2 , C-C single bond length $r(C_1 - C_2) = 1.524 \pm 0.008$ Å (table 7, column II) should be compared with 1.501 ± 0.005 Å in acetaldehyde,²⁸ 1.507 ± 0.003 Å in acetone,³⁰ 1.527 ± 0.003 Å in cyclobutanone ³ and 1.522 ± 0.002 Å in oxetanone.³¹ The agreement among the strained cyclic ketone systems is striking. Similarly, $r(C_2-C_3) =$ 1.509 ± 0.005 Å is characteristic of C--C single bonds attached to ethylenic groups; for example 1.501 ± 0.004 Å and 1.509 ± 0.005 Å are the corresponding values for propene ³² and cyclopentadiene.³³ The ethylene group parameters of cyclopent-3enone are essentially identical with the r_0 -parameters of ethylene,³⁴ while r(C=0) =1.210±0.002 Å is near to those of acetone,³⁰ acetaldehyde ²⁸ and formaldehyde.³⁵ A discussion of the methylene group parameters for cyclopent-3-enone is unprofitable since they depend critically on both small coordinates, $a(C_2)$ and $a(H_2)$, and in consequence are probably not well determined.

The ring angles of cyclopent-3-enone indicate that the angle strain required to close the ring is fairly evenly distributed, for the 120° angles at the sp^2 hybridised carbon atoms are decreased by about 10° at C_1 and about 8° for each of C_3 and $C_{3'}$ while the angles at the sp^3 hybridised carbon atoms, C₂ and C_{2'}, are decreased from 109° 28' by about 6.5°. Similar behaviour is exhibited by the isoelectronic vinylene carbonate.³⁶

A number of related ketones have dipole moments similar to the value of $\mu =$ 2.79 ± 0.03 D exhibited by cyclopent-3-enone. For example, the values for cyclobutanone,³ acetone ³⁷ and cyclohexanone ³⁸ are 2.89 ± 0.03 , 2.90 and 2.87 ± 0.04 D respectively. The dipole moments of cyclopentanone¹⁵ ($\mu = 3.25 \pm 0.02$ D) and bicyclo[2, 1, 1]hexan-2-one ³⁹ ($\mu_a = 3.32 \pm 0.02$ D) do not fall into this pattern.

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