Studies on Molecules with Five-membered Rings

I. Calculation of Conformational Energies for Tetrahydrofuran and 1,2,4-Trioxacyclopentane

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Conformational energies have been calculated for tetrahydrofuran and 1,2,4-trioxacyclopentane by the Westheimer-Hendrickson method. Results for various choices of the necessary constants are given. The difference in energy between the conformations with C_s and C_2 symmetry is found to be between 0.81 and 1.29 kcal/mole for 1,2,4-trioxacyclopentane. (The C_2 conformation is the more stable form). The C_s and C_2 conformations of tetrahydrofuran have probably nearly the same energy; the difference was found to be between -0.73 and $+1.25$ kcal/mole. The results of these calculations are used in electron diffraction investigations of the compounds published in following papers.

The information available about the structures of cyclopentane analogues in the gaseous state is limited. Cyclopentane itself has been studied by electron diffraction.[1] The C—C bond length was found to be 1.539 Å in close agreement with the C—C distance in ethane. The ring is not planar because of the great torsional strain (Pitzer strain) in the planar conformation.[2,3] The two non-planar forms with the highest symmetry are the "half-chair" (C_2 symmetry) and the "envelope" (C_s symmetry) conformations.[2-4] Pitzer *et al.*[2,3] showed that these two conformations as well as intermediate conformations, have nearly the same energy. Cyclopentane is therefore not found in one well defined conformation. At one instant a particular part of the molecule has the greatest puckering, but the puckering moves around the ring continuously (pseudo-rotation).

Pitzer *et al.*[2,3] described the pseudo-rotation by the following equation for the z-coordinates

$$z_j = \sqrt{\tfrac{2}{5}}\, q \cos\left[2(72^\circ \cdot j + \varphi)\right] \qquad (1)$$
$$(j = 0, 1, 2, 3, 4)$$

Here q is the amplitude of the puckering, and φ the phase angle of maximum puckering. The C_s conformation is obtained for $\varphi = 0$ (or in general for

$\varphi = l \times 18°$ where l is an integer) and the C_2 conformation for $\varphi = (2l+1) \times 9°$.
Altona et al.[5,6] have described the pseudo-rotation by

$$\varphi_j = \varphi_m \cos[(\varDelta/2) + j\delta] \qquad (2)$$
$$j = 0, 1, 2, 3, 4 \text{ and } \delta = 144°$$

φ_j is here the torsional angle around the j'th bond in the ring (see Fig. 1).
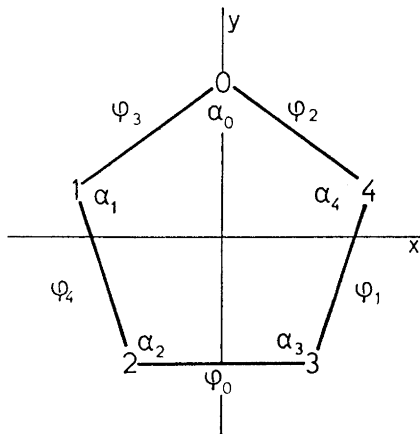φ_m is a constant equal to the maximum possible torsional angle.

Fig. 1. The numbering of the atoms, bond angles and torsional angles applied to the five-membered ring.

For symmetrical cyclopentane analogues one would expect the minimum in potential energy to correspond closely either to the "half-chair" or to the "envelope" conformation, and the energy minimum may be so deep that the molecule is effectively in one definite conformation. Pitzer and Donath [3] used barriers to internal rotation known from related molecules to estimate the energy difference between the C_2 and the C_s conformations of some cyclopentane derivatives. By using the barriers found in methanol (1.07 kcal/mole [7]) for the C—O bonds, they estimated that the "half-chair" of tetrahydrofuran (THF) should be about 2.5 kcal/mole more stable than the envelope conformation. Later Lafferty et al.[8] found that the far infrared spectrum of THF gave evidence for pseudo-rotation in this compound, and they estimated the energy difference between the two symmetric forms to be less than 0.5 kcal/mole. Further spectroscopic work (microwave) by Gwinn et al. (see Ref. 9) has also been interpreted in terms of essentially free pseudo-rotation.

Some five-membered rings including THF,[10] tetrahydrothiophene,[11] and 1,2,4-trioxacyclopentane (TOCP)*[12] are now being studied by electron diffraction in this laboratory. In the case of THF it was first attempted to obtain agreement between experimental and theoretical intensity and radial distribution curves by assuming C_2 symmetry. However, with this assumption reasonably good agreement could only be obtained if some of the angles and some

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* The usual numbering of the atoms has been kept in this name.

of the root-mean-square amplitudes of vibration were given very unreasonable values.[10] The energy calculations described below were carried out to obtain reasonable theoretical models to use in the electron diffraction investigation.

THE WESTHEIMER-HENDRICKSON METHOD FOR CALCULATION OF CONFORMATIONAL ENERGIES

Conformational energies were calculated according to the method first applied by Westheimer [13] and later used in various versions by others.[4,14-16] The conformational energy corresponding to a molecular model may approximately be written as a sum of terms, i.e.

$$E = E^f + E^a + E^t + E^v \qquad (3)$$

E^f is the sum of compression and stretching energies required to change the bond lengths from their "normal" values to the values they actually have in the molecule in question. E^a is a corresponding sum of bending energies required to change the bond angles. E^t is the sum of the torsional strain energies, and E^v is the van der Waals energy due to the interaction between non-bonded atoms. The terms from pairs of atoms bound to the same atom are neglected.

The zero-point vibrational energy is not included in the energy expression. The effect on the energy differences will probably be small.[3]

In the present case the term E^f has been neglected. The inclusion of E^f is usually not too important,[4] and the results are in any case only rough approximations because of the difficulty in estimating the constants necessary for the calculation of the other terms. The bond lengths were taken from preliminary electron diffraction results (cf. Table 1).

In most of the calculations of this type it is assumed that a simple Hooke's law potential may be applied for the bending energy, i.e.

$$E_i^a = \tfrac{1}{2}k_i\,(\theta_i - \theta_i^0)^2 \qquad (4)$$

where k_i is the force constant and θ_i^0 is the "normal" value for the i'th angle. Experience has shown that the expression (4) gives rather too high values for E_i^a. A different analytical expression may be used,[16] or eqn. (4) may be applied with a force constant which is somewhat lower than the value obtained by normal coordinate analysis for the type of bond angle in question.

The usual expression

$$E_i^t = \tfrac{1}{2}V_i^0\,(1 + \cos 3\varphi_i) \qquad (5)$$

where φ is the torsional angle, was used for the C—C and C—O bonds. The contribution from the O—O bond in TOCP to E^t has been calculated by using the potential function found in H_2O_2,[17] which corresponds to a barrier of 7.03 kcal/mole in the cis conformation ($\varphi=0$) and 1.10 kcal/mole in the trans conformation; the minimum in the potential was found to be at $\varphi=111.5°$.

The necessary constants in the expressions (4) and (5) must be taken from related molecules. While reasonable sets of constants have been established for hydrocarbons,[4,13-16] little work has been done on other molecules. The bending force constant k_{CCC} is usually found to be about 0.035 kcal/mole

degree[2] (Ref. 4). The proper value for k_{CCO} is probably not too different from this value, though it may be somewhat higher.[18] A recent investigation of dimethylether[19] gave 0.049 kcal/mole degree[2] for k_{COC}.

The CCC angles in propane,[20] butane,[21,22] and pentane[23,24] are between 112 and 113°. A value closer to the tetrahedral angle is often used in energy calculations of the type discussed here.[16] In dimethylether the COC angle is about 111.5°.[25,26]

The barriers V_{CC}^0 (eqn. (5)) were taken from ethane[4,27] (2.9 kcal/mole). The barriers to rotation about the C—O bonds in methanol and dimethylether are very different, namely 1.07 kcal/mole[7] and 2.72 kcal/mole,[26] respectively. Various values have therefore been tried for V_{CO}^0.

The last term in (4) (E^v) has been calculated as described by Eliel et al.[4] with the constants given on p. 452 of their book. The inclusion of this term was of very little importance.

THE COMPUTER PROGRAM

The energy calculations were carried out on a CDC 3300 computer. The program was written in FORTRAN.

All the HCH angles were assumed equal, and the planes through HCH were assumed perpendicular to the planes through XCC (X=O or C), bisecting the XCC angle. The HCH angles were kept at a fixed value in each calculation.[4,14]

The four angles α_0, α_1, φ_2, and φ_3 (see Fig. 1) were taken as independent parameters. These four angles could be adjusted to find the minimum in energy, or φ_2 could be kept at a fixed value while the three other angles were adjusted. The minimum was found by the method of the steepest descent. The derivatives were calculated numerically usually by giving the angles shifts of 0.005 degrees. If a shift of +0.005 degrees gave a lowering in energy the derivative was calculated immediately. When an increase in energy was found a shift of —0.005 was tried. If the energy decreased the derivative was calculated, otherwise this derivative was put equal to zero. When all the derivatives became zero in this way, it was assumed that the energy minimum had been found. The procedure gave quite insignificant variation in the final parameters for different starting values.

RESULTS AND DISCUSSION

Table 1 give the conformational energies found for THF and TOCP for some sets of constants in the energy expression (3).

For each set of constants the results are given for six conformations. The first one (conformation I) has nearly C_2 symmetry and the last one (conformation VI) nearly C_s symmetry. The energies found for the intermediate conformations II—V were obtained by finding the energy minima for fixed values of the angles φ_2. φ_2 was fixed so that the torsional angles should approximately satisfy the relations which hold for a cyclopentane model with C_s or C_2 symmetry.* Thus the conformations I—VI correspond approximately to

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* φ_2 was usually changed in steps of 1°.

Table 1. Conformational energies, *cf.* eqn. (3), (in kcal/mole) and the corresponding angle parameters (in degrees) in THF and TOCP.

Conformation angles		Tetrahydrofuran						1,2,4-Trioxacyclopentane		
		a	b	c	d	e	f	g	h	i
I (approx. C_2 sym.)	α_0	109.5	109.7	109.5	109.6	108.8	108.1	106.5	107.3	107.6
	α_1	106.8	106.7	106.7	106.8	106.6	107.2	105.3	106.2	106.8
	φ_2	13.0	13.0	13.2	12.6	14.2	13.7	15.7	13.4	11.8
	φ_3	12.4	12.4	12.6	12.4	13.7	13.7	15.6	13.7	11.8
	E	10.07	10.09	11.32	8.41	8.14	8.28	10.08	12.70	10.17
II	α_0	109.3	109.5	109.2	109.4	108.5	107.9	106.2	107.0	107.4
	α_1	105.6	105.5	105.5	105.7	105.1	106.1	103.5	105.0	106.0
	φ_2	0.0^a	0.0^a	0.0^a	0.0^a	0.0^a	0.0^a	0.0^a	0.0^a	0.0^a
	φ_3	24.2	24.1	24.7	23.5	26.5	26.0	29.2	24.9	21.8
	E	10.10	10.12	11.25	8.56	8.16	8.34	10.29	12.83	10.31
III	α_0	108.6	108.9	108.5	108.8	107.7	107.2	105.2	106.3	106.9
	α_1	104.5	104.3	104.3	104.7	103.8	104.9	102.2	104.3	105.4
	φ_2	-12.0^a	-12.0^a	-12.0^a	-12.0^a	-13.0^a	-13.0^a	-14.0^a	-12.0^a	-10.0^a
	φ_3	32.8	32.7	33.4	32.0	35.9	35.0	38.4	32.7	28.2
	E	10.16	10.18	11.08	8.91	8.18	8.47	10.69	13.10	10.56
IV	α_0	107.5	107.8	107.4	107.7	106.4	106.1	103.8	105.4	106.2
	α_1	103.8	103.6	103.6	104.1	102.9	104.4	102.0	104.2	105.4
	φ_2	-24.0^a	-24.0^a	-24.0^a	-23.0^a	-26.0^a	-24.5^a	-27.0^a	-22.0^a	-19.0^a
	φ_3	39.1	38.9	39.7	37.7	42.8	40.6	44.1	37.0	32.0
	E	10.22	10.26	10.86	9.31	8.19	8.59	11.09	13.33	10.92
V	α_0	106.4	106.8	106.2	106.7	104.9	105.1	102.6	104.6	105.8
	α_1	104.2	104.0	103.9	104.9	103.3	104.7	103.0	104.8	106.1
	φ_2	-33.0^a	-33.0^a	-34.0^a	-32.0^a	-36.5^a	-34.0^a	-36.0^a	-30.0^a	-25.0^a
	φ_3	41.2	41.0	42.3	39.3	45.4	42.5	45.1	38.0	31.9
	E	10.24	10.32	10.67	9.60	8.17	8.64	11.31	13.47	11.13
VI (approx. C_s sym.)	α_0	105.9	106.4	105.4	106.9	104.3	104.7	102.4	104.4	106.6
	α_1	105.4	105.1	104.8	106.2	104.7	105.8	104.9	106.1	107.6
	φ_2	-39.4	-38.7	-41.3	-35.0^b	-43.5	-40.2^b	-41.5^b	-34.9^b	-24.6^b
	φ_3	39.0	38.7	41.3	35.0	43.3	40.2	41.5	34.9	24.6
	E	10.25	10.33	10.59	9.66	8.15	8.64	11.37	13.51	11.16

^{a} Not varied.
^{b} Energy minimum with restriction of C_s symmetry.

Below k is given in kcal/mole degree ^{2} and V° in kcal/mole.

Tetrahydrofuran

Bond distances: $r(CO) = 1.426$ Å, $r(CC) = 1.539$ Å, $r(CH) = 1.113$ Å, $\angle HCH = 112°$

a: $\theta_{COC}{}^\circ = \theta_{OCC}{}^\circ = \theta_{CCC}{}^\circ = 112°$
   $k_{COC} = k_{OCC} = k_{CCC} = 0.030$; $V_{CO}{}^\circ = 2.0$, $V_{CC}{}^\circ = 2.9$
b: $\theta_{COC}{}^\circ = \theta_{OCC}{}^\circ = \theta_{CCC}{}^\circ = 112°$
   $k_{COO} = 0.035$, $k_{OCC} = k_{CCC} = 0.030$; $V_{CO}{}^\circ = 2.0$, $V_{CC}{}^\circ = 2.9$

Table 1. Continued.

c: $\theta_{COC}^0 = \theta_{OCC}^0 = \theta_{CCC}^0 = 112°$
　$k_{COC} = k_{OCC} = k_{CCC} = 0.030;$ $V_{CO}^0 = 2.7,$ $V_{CC}^0 = 2.9$
d: $\theta_{COC}^0 = \theta_{OCC}^0 = \theta_{CCC}^0 = 112°$
　$k_{COC} = k_{OCC} = k_{CCC} = 0.030;$ $V_{CO}^0 = 1.07,$ $V_{CC}^0 = 2.9$
e: $\theta_{COC}^0 = 109°,$ $\theta_{OCC}^0 = \theta_{CCC}^0 = 110°$
　$k_{COC} = k_{OCC} = k_{CCC} = 0.030;$ $V_{CO}^0 = 2.0,$ $V_{CC}^0 = 2.9$
f: $\theta_{COC}^0 = 109°,$ $\theta_{OCC}^0 = \theta_{CCC}^0 = 110°$
　$k_{COC} = k_{CCO} = 0.45,$ $k_{CCC} = 0.030;$ $V_{CO}^0 = 2.0,$ $V_{CC}^0 = 2.9$

Trioxacyclopentane

Bond distances $r(CO) = 1.414$ Å, $r(OO) = 1.488$ Å, $r(CO) = 1.115$ Å, $\angle HCH = 112°$

g: $\theta_{COC}^0 = 109°,$ $\theta_{OCO}^0 = 110°,$ $\theta_{COO}^0 = 106°$
　$k_{COC} = 0.035,$ $k_{OCO} = 0.030,$ $k_{COO} = 0.035;$ $V_{CO}^0 = 2.0$
h: $\theta_{COC}^0 = \theta_{OCO}^0 = 112°,$ $\theta_{COO}^0 = 109°$
　$k_{CCO} = k_{OCO} = k_{COO} = 0.035;$ $V_{CO}^0 = 2.0$
i: $\theta_{CCO}^0 = \theta_{OCO}^0 = 112°,$ $\theta_{COO}^0 = 109°$
　$k_{CCO} = k_{OCO} = k_{COC} = 0.035;$ $V_{CO}^0 = 1.07$

values for φ in eqn. (1) equal to $l \times 9°$ and to values for $\varDelta$ in eqn. (2) approximately equal to $l \times 36°$.

The $\varDelta$ values [5,6] are given below:

Conformation　　I: $\varDelta = 0°$　　　　(equivalent to $\varDelta = 360°$)
　　　　》　　　II: $\varDelta = 684°$　　　(　　》　　　》 $\varDelta = 36°, 324°, 396°$)
　　　　》　　　III: $\varDelta = 648°$　　(　　》　　　》 $\varDelta = 72°, 288°, 432°$)
　　　　》　　　IV: $\varDelta = 612°$　　(　　》　　　》 $\varDelta = 108°, 252°, 468°$)
　　　　》　　　V: $\varDelta = 576°$　　(　　》　　　》 $\varDelta = 144°, 216°, 504°$)
　　　　》　　　VI: $\varDelta = 540°$　　(　　》　　　》 $\varDelta = 180°$)

　　For THF the energy minimum corresponds to a model with approximately C_2 symmetry (conformation I) except when $V_{CO}^0 = 2.7$ kcal/mole (column c), which gives a minimum for a model with approximately C_s symmetry. The energy difference between the conformation VI and conformation I is small if $V_{CO}^0 = 2.0$ kcal/mole (columns a, b, c, and f), and 1.25 kcal/mole for $V_{CC}^0 = 1.07$ kcal/mole (column d). A local minimum was often found for conformation VI. The difference between the angles in the first four columns is seen to be quite small.

　　The energy minimum for TOCP was found for a model with nearly C_2 symmetry. The conformation VI has 1.29, 0.81, and 0.99 kcal/mole higher energy in the three columns.

　　The energy difference between the C_s and the C_2 models becomes smaller if θ_{COO}^0 is increased. The C_2 model is for example only slightly more favourable than the C_s model if $\theta_{COO}^0 = 112°$ and the other constants are as given in Table 1h. However, the structures corresponding to the calculated energy

minima are then in very bad agreement with the structures consistent with the electron diffraction data.[12]

The results indicate that the C_2 and C_s conformations of THF do not differ much in energy. It is more likely that TOCP exists predominantly in a conformation with C_2 symmetry. These results seem to be in agreement with the electron diffraction results for these molecules.[10,12]

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