ACTA CHEMICA SCANDINAVICA **23** (1969) 3398–3406

Studies on Molecules with Five-membered Rings

III. An Electron Diffraction Investigation of Gaseous 1,2,4-Trioxacyclopentane (Ethylene ozonide)

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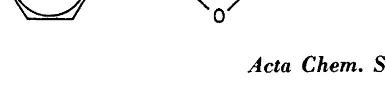
Gaseous 1,2,4-trioxacyclopentane has been studied by electron diffraction. A model with C_2 symmetry gives very satisfactory agreement between theoretical and experimental intensity values. Results and standard deviations for the most important molecular parameters are as follows.

Bond distances: $r_a(\mathrm{C-O})=1.414_5$ (0.0025) Å, $r_a(\mathrm{O-O})=1.487 \left\{\begin{matrix}+0.004\\-0.006\end{matrix}\right\}$Å, $r_a(\mathrm{C-H})=1.126$ (0.011) Å. Bond angles: $\angle\mathrm{COC}=105.9(1.1)^\circ$, $\angle\mathrm{OCO}=105.3(0.8)^\circ$, $\angle\mathrm{COO}=99.2(0.7)^\circ$. Torsional angles: $\phi(\mathrm{C_3-O_4})=16.2(0.6)^\circ$, $\phi(\mathrm{C_3-O_2})=-40.2(1.3)^\circ$, $\phi(\mathrm{O-O})=49.1(1.5)^\circ$.

It is possible, however, to obtain an almost equally good agreement between theoretical and experimental intensities by assuming C_s symmetry, but calculations of conformational energies favour the C_2 model, as various sets of potential constants give energy differences in the range 1.45–3.14 kcal/mole.

The stability of a conformation of a five-membered ring is to a great extent determined by torsional strain (Pitzer strain).[1] The first paper[2] of this series gives conformational energies for tetrahydrofuran (THF) and 1,2,4-trioxacyclopentane (TOCP). The results indicated nearly free pseudo-rotation in THF, while TOCP may well exist effectively in the "half-chair" conformation with C_2 symmetry (see Fig. 1). The electron diffraction investigation of THF gave further evidence for nearly free pseudo-rotation in THF.[3]

1,2,4-Trioxacyclopentane has been studied by electron diffraction by W. Shand (see Ref. 4). The ring was found to be non-planar with an average bond distance of 1.44 Å and an average bond angle of about 103°. An X-ray investigation of 3-carbmethoxy-5-anisyl-1,2,4-trioxacyclopentane



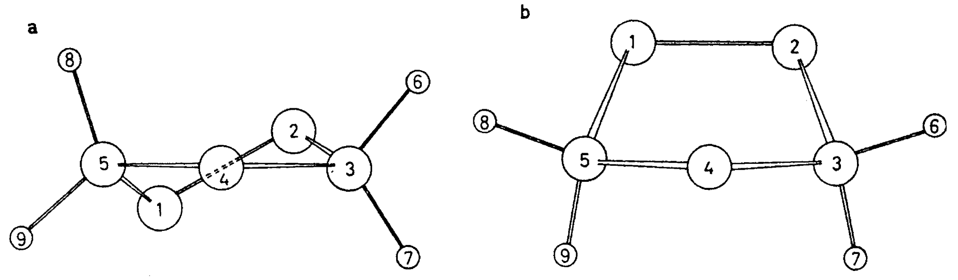


Fig. 1a. The "half-chair" conformation (with C_2 symmetry). Atom 1 is below and atom 2 above the plane through the atoms 3, 4, and 5.
b. The "envelope" conformation (with C_s symmetry). The atoms 1 and 2 are both above the plane through the atoms 3, 4, and 5.

is now being carried out by P. Groth [5] at this university. He has also studied a number of cyclic peroxides.[6]

EXPERIMENTAL

1,2,4-Trioxacyclopentane was synthetised from ethylene and ozone. Various solvents were tried (pentane, methylene chloride, and methyl chloride). Criegee *et al.*[7] have applied methyl chloride in synthetising derivatives of 1,2,4-trioxacyclopentane, and a similar procedure was adopted. The compound is a colourless liquid at room temperature and must be handled with care to avoid explosion.

The NMR spectrum showed that the sample did not contain a significant amount of the solvent. The resonance frequencies for hydrogen are normal, and the four hydrogen atoms are equivalent on the NMR time scale.

The electron diffraction pictures were taken in the usual way with the Oslo apparatus.[8] The nozzle temperature was about 15°C and the electron wave length 0.0648 Å. Photographs were taken at two nozzle-to-plate distances, *i.e.* about 47.9 and 20.7 cm. The data were handled as the data for THF.[3]*

STRUCTURE ANALYSIS

The average molecular intensity covered the s-range 2.0—42.5 Å^{-1}. This experimental intensity is shown in Fig. 2 and the corresponding radial distribution function in Fig. 3. The small inner peak (near 1.1 Å) in the RD curve corresponds to the C—H bonds. The high, narrow peak near 1.45 Å contains contributions from the C—O and O—O bond distances. The small half-width of this peak shows that the bond distances cannot be very different. The main contributions to the next peak are from the non-bonded distances in the ring. Non-bonded O···H and C···H distances give contributions in the interval 2.10—3.30 Å.

Rough estimates of the interatomic distances were obtained from the RD curve. Least-squares calculations on the intensity data were then carried out.[9]

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[*] The procedure applied in this investigation is described by Andersen *et al.*[9] Most of the applied formulas are also given in the review article by Seip.[10] The scattering amplitudes applied in the study of THF [3] were also used in the present study.

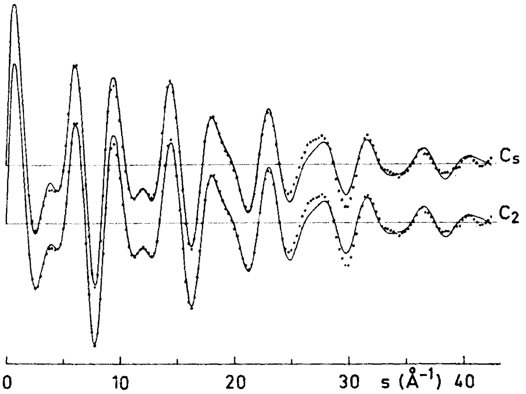

Fig. 2. The experimental intensity curve (dotted) compared to the theoretical curves calculated for the C_s and the C_2 conformations.

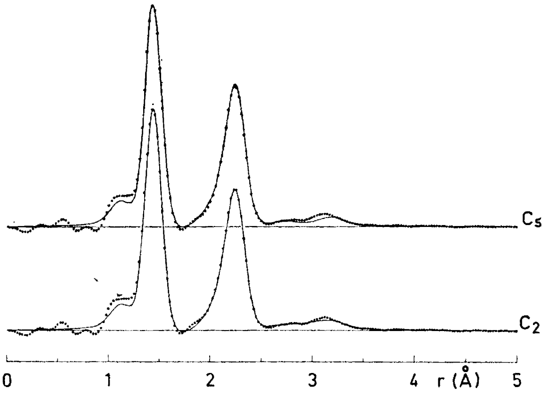

Fig. 3. The experimental RD curve (dotted) compared to theoretical curves calculated for the C_s and C_2 conformations. Artificial damping constant,[9] $k = 0.002$ Å^2.

The H atoms in each CH_2 group were assumed to be situated symmetrically with respect to the neighbouring atoms. The C—O bond distances were assumed equal.

The results * obtained based on a C_2 model are given in Table 1 columns a and b. The root-mean-square amplitudes $u(O\cdots O)$, $u(C\cdots C)$, and $u(C...O)$ were first assumed equal. With this assumption convergence was not obtained without an additional restriction. A series of calculations was therefore carried out with slightly different values for $\angle$COC. In each refinement this angle

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* The distances may be denoted by r_a[11] which is equivalent to $r_g(1)$.[12]

Table 1. Structure parameters obtained by least-squares refinement on the intensity data. Distances (r_a values) and root-mean-square amplitudes of vibration (u) in Å, angles in degrees. The standard deviations given in parentheses are those obtained in the least-squares calculations without corrections.

With the restriction $u(\mathrm{O}\cdots\mathrm{O})=u(\mathrm{C}\cdots\mathrm{O})=u(\mathrm{C}\cdots\mathrm{C})$ the parameters refined to the values in a and c, while the results in b and d were obtained without this restriction. The u values for the bond distances were assumed equal ($u(\mathrm{X-O})$). $u(\mathrm{O}_4\cdots\mathrm{H})$ was kept constant at 0.13 Å. The u values for the other O···H and C···H distances were assumed equal and refined ($u(\mathrm{X}\cdots\mathrm{H})$ in the table).

	C_2 symmetry		C_s symmetry	
	a	b	c	d
$r(\mathrm{C-O})$	1.414_5 (0.0008)	1.414_4 (0.0008)	1.414_4 (0.0008)	1.414_3 (0.0008)
$r(\mathrm{O-O})$	1.487_1 (0.0042)	1.487_3 (0.0041)	1.486_3 (0.0041)	1.487_0 (0.0042)
$r(\mathrm{C-H})$	1.127 (0.011)	1.126 (0.011)	1.122 (0.011)	1.123 (0.011)
∠COC	105.5 (5.1)	105.9 (1.0)	98.4 (0.5)	98.1 (0.6)
∠OCO	105.7 (2.9)	105.3 (0.7)	103.8 (0.2)	104.1 (0.4)
∠HCH	116.7 (6.6)	112.3 (6.8)	117.8 (4.8)	117.2 (5.3)
$u(\mathrm{X-O})$	0.042_7 (0.0015)	0.042_7 (0.0015)	0.042_6 (0.0015)	0.042_5 (0.0015)
$u(\mathrm{C-H})$	0.086 (0.010)	0.086 (0.010)	0.086 (0.010)	0.086 (0.010)
$u(\mathrm{O}\cdots\mathrm{O})$	0.062_8 (0.0114)	0.052 (0.003)	0.050_5 (0.0023)	0.048 (0.004)
$u(\mathrm{C}\cdots\mathrm{C})$		0.099 (0.068)		0.049 (0.013)
$u(\mathrm{C}\cdots\mathrm{O})$		0.077 (0.022)		0.059 (0.008)
$u(\mathrm{X}\cdots\mathrm{H})$	0.114 (0.040)	0.125 (0.046)	0.104 (0.025)	0.111 (0.029)
$\sum W\Delta^2$	1.0435	1.0000	1.0304	1.0197

was kept constant. The results given in Table la correspond to the minimum in

$$S = \sum_s W_s \, \Delta_s^2$$

obtained in this way. (The sum is over all observations, W_s is the weight on observation s, and $\Delta_s = I_s^{\mathrm{obs}} - \mathrm{Scale} \times I_s^{\mathrm{calc}}$). An attempt was made to refine ∠COC in addition to the other parameters using the results in Table la as starting values. Convergence was not achieved, but the values obtained as standard deviations in the first cycle, are given in Table la.

Slightly different results were obtained by treating $u(\mathrm{O}\cdots\mathrm{O})$, $u(\mathrm{C}\cdots\mathrm{C})$, and $u(\mathrm{C}...\mathrm{O})$ as independent parameters (Table 1b). It was then possible to refine simultaneously all the parameters given in the table. The sum S is of course lower than in column a.

The results in Table 1c and d were obtained by assuming C_s symmetry. With the restriction $u(\mathrm{O}\cdots\mathrm{O})=u(\mathrm{C}\cdots\mathrm{C})=u(\mathrm{C}\cdots\mathrm{O})$ the parameters refined to the values given in column c. The sum S is in fact slightly lower in column c than in column a. Without this restriction the results in column d were obtained. S is slightly higher in this column than in column b.

The standard deviations for some of the parameters (*e.g.* ∠COC and ∠OCO) are considerably greater in column b than in column d. The reason is found in the difference in the correlation matrices.[9] For example, the correlation coefficient between the parameters ∠COC and ∠OCO is -0.88 for C_2 symmetry and -0.17 for C_s symmetry.

The theoretical intensity and RD curves calculated for the parameters in Table 1b and Table 1d, are compared to the corresponding experimental curves in the Figs. 2 and 3. The difference between the theoretical curves corresponding to the C_2 and to the C_s model is quite small. However, the RD curve calculated with the C_2 model agrees slightly better with the experimental curve in the outer part.

ENERGY CALCULATIONS

The conformational energies for TOCP published in the first paper of this series,[2] indicated that the "half-chair" conformation (C_2 symmetry) was more stable than the "envelope" conformation (C_s symmetry). The angles corresponding to minima in conformational energies for four sets of constants are compared to the experimental values in Table 2 (*cf.* Ref. 2). The agreement

Table 2. Calculated and experimental bond angles and torsional angles. The calculated values in the columns a-d correspond to minima in conformational energy. The columns a-c correspond to the columns g-i of Table 1 in Ref. 2. The calculations were not carried out under the assumption of C_2 symmetry. However, angles which are equal in a C_2 model, did never differ by more than 0.06°.

	Calculated				Exptl.	
	a	b	c	d	C_2	C_s
∠COC	106.5	107.3	107.6	106.9	105.9	98.1
∠OCO	105.3	106.2	106.8	105.9	105.3	104.1
∠COO	99.8	101.7	102.9	101.0	99.2	103.3
$\phi(C_3-O_4)$	15.7	13.4	11.8	14.3	16.3	49.4
$\phi(C_3-O_2)$	−38.8	−33.3	−29.3	−35.5	−40.2	−30.8
$\phi(O-O)$	47.5	40.8	36.0	43.5	49.1	0.0

The potential for rotation around the O−O bond was the same in all the calculations.[13] The other potential constants [2] were (k is given in kcal/mole degree [2] and $V°$ in kcal/mole):

a: $\theta_{\mathrm{COC}}{}^{\circ}=109^{\circ}$, $\theta_{\mathrm{OCO}}{}^{\circ}=110^{\circ}$, $\theta_{\mathrm{COO}}{}^{\circ}=106^{\circ}$
$k_{\mathrm{COC}}=0.035$, $k_{\mathrm{OCO}}=0.030$, $k_{\mathrm{COO}}=0.035$; $V_{\mathrm{CO}}{}^{\circ}=2.0$

b: $\theta_{\mathrm{COC}}{}^{\circ}=\theta_{\mathrm{OCO}}{}^{\circ}=112^{\circ}$, $\theta_{\mathrm{COO}}{}^{\circ}=109^{\circ}$
$k_{\mathrm{COC}}=k_{\mathrm{OCO}}=k_{\mathrm{COO}}=0.035$; $V_{\mathrm{CO}}{}^{\circ}=2.0$

c: $\theta_{\mathrm{COC}}{}^{\circ}=\theta_{\mathrm{OCO}}{}^{\circ}=112^{\circ}$, $\theta_{\mathrm{COO}}{}^{\circ}=109^{\circ}$
$k_{\mathrm{COC}}=k_{\mathrm{OCO}}=k_{\mathrm{COC}}=0.035$; $V_{\mathrm{CO}}{}^{\circ}=1.07$

d: $\theta_{\mathrm{COC}}{}^{\circ}=\theta_{\mathrm{OCO}}{}^{\circ}=112^{\circ}$, $\theta_{\mathrm{COO}}{}^{\circ}=109^{\circ}$
$k_{\mathrm{COC}}=k_{\mathrm{OCO}}=k_{\mathrm{COC}}=0.035$; $V_{\mathrm{CO}}{}^{\circ}=2.70$

between the experimental C_2 model and the theoretical models is reasonably good, especially the theoretical values in column a are quite close to the observed angles.

The conformation energies calculated with the molecular parameters in Table 1b and are given in Table 3. The "envelope" conformation is found to be less stable than the "half-chair"; the smallest energy difference being about 1.5 kcal/mole (column d).

The energies given in Table 3 may possibly be improved by including the electrostatic energy between point charges on the atoms. Net atomic charges were therefore estimated as described by Whitehead *et al.*[23] Neclecting the charges on the H atoms, the energy difference between the two models increased by about 1 kcal/mole.

It seems questionable if the inclusion of the interaction between point charges is sufficiently accurate for atoms with lone pairs. The so called "rabbit-ear effect" discussed by Eliel,[24] may be important, and would probably lead to still larger energy differences.

Table 3. Conformational energies (in kcal/mole) calculated with the potential constants in Table 2 a-d. The values given in the first row are the energy minima corresponding to the molecular parameters in Table 2 a-d. The values in the second and third row were obtained with the molecular parameters given in Table 1b and d, respectively.

	a	b	c	d
C_2 symmetry	10.08	12.70	10.17	14.46
	10.11	13.25	11.26	14.76
C_s symmetry	12.10	15.43	14.40	16.21

DISCUSSION

This investigation does not completely settle the conformational problem of TOCP. Molecular models with C_2 and C_s symmetry both give reasonably good agreement between experimental and theoretical intensity- and RD curves (Figs. 2 and 3). Models without any symmetry element have not been tried in least-squares refinements. Since both C_2 and C_s models give good agreement between experimental and theoretical intensities, a similar agreement could probably be obtained also with a less symmetric model. A mixture of conformations corresponding to free or restricted pseudo-rotation [2,3] may also give nearly the same intensity- and RD curves.

The electron diffraction data alone thus gives scant evidence for preferring the C_2 conformation. The agreement in the outer part of the RD curves is slightly better for the C_2 than for the C_s model. In addition the COC angle refines to a value which seemes unreasonably small if C_s symmetry is assumed (Table 1). The calculated conformational energies (Table 3) give further support to the conclusion that TOCP exists predominantly in the C_2 conformation. However, if the potential assumed for rotation around the O—O bond [13] is seriously wrong, these results are worthless. We plan to solve the conformational problem by studying a suitable derivative of TOCP.

It is difficult by means of electron diffraction to obtain really accurate bond distances in TOCP, since there are actually three different bond distances of nearly the same length. The standard deviation for the O—O bond is rather large, since the contribution from the C—O distances is about four times larger (Table 1). The *u* values obtained for the bond distances seem to be slightly lower than one would expect.[3,14] With the *u* value fixed at 0.05 Å the O—O and C—O distances refined to 1.418 Å and 1.464 Å, resp. The sum *S* (p. 3401) was considerably higher (1.147) than the values in Table 1. Even though, an O—O bond longer than 1.487 Å seems less probable than a shorter one. The opposite holds true for the C—O distance. The standard deviations given in Table 1 are probably too small, since a diagonal weight matrix was applied in the least-squares calculations.[15] The uncertainty in the electron wave length should also be included in the standard deviations for the distances. Table 4 gives our final results for the most important molecular parameters. The COO angle and torsional angles which were treated as dependent parameters, are also included in the table.

The O—O bond length given in Table 4 is somewhat longer than the O—O bond in H_2O_2, which was found to be 1.475 Å by Redington *et al.*[16] (from the IR spectrum) and 1.453±0.007 Å by Busing and Levy[17] (neutron diffraction). Groth[6] has by X-ray diffraction found O—O bond lengths in the range 1.472—1.482 in various cyclic peroxides.

Table 4. Final results for the most important distances, root-mean-square amplitudes (in Å) and angles (in degrees). Standard deviations are given in parentheses.

r_a (C—O)	1.414_5	(0.002_5)	∠COC	105.9	(1.1)
r_a (O—O)	1.487	$\left\{\begin{matrix}+0.004\\-0.006\end{matrix}\right\}$	∠OCO	105.3	(0.8)
r_a (C—H)	1.126	(0.011)	∠COO	99.2	(0.7)
u (C—O)	0.043	(0.002)	$\phi(C_3-O_4)$	16.2	(0.6)
u (O—O)			$\phi(C_3-O_2)$	−40.2	(1.3)
u (C—H)	0.086	(0.010)	ϕ(O—O)	49.1	(1.5)

Our value for the O—O bond is significantly longer than that obtained by Busing and Levy according to the given error estimates. Still one may question if the difference is real, since the IR investigation gave an O—O bond length in better agreement with our result. However, there may well be different O—O bond lengths in H_2O_2 and TOCP. The bond angles are not identical, and the torsional angle in TOCP seems consistent with a slightly longer O—O bond.

The CO bond lengths found in some compounds are given below:

	Bond length (Å)	Method	Ref.
Methanol	1.428	E.D.	18
	1.427	M.W	19
Dimethylether	1.416	E.D.	18
	1.417	M.W	20
1,2,4-Trioxacyclopentane	1.414_5	E.D.	this work
Tetrahydrofuran	1.428	E.D.	3
s-Trioxane	1.409	E.D.	21
	1.411	M.W.	22
Cyclic peroxides	1.41 – 1.446 (usually near 1.44)	X.D.	6

(E.D.: electron diffraction; M.W.: microwave spectroscopy; X.D.: X-ray diffraction).

The value obtained in this investigation is seen to be very nearly the same as found in dimethylether and in *s*-trioxane. The difference between the CO bond lengths in TOCP and THF may be related to the difference in net charges on the atoms.

Note added in proof. The investigation of 3-carbmethoxy-5-anisyl-1,2,4-trioxacyclopentane is now completed.[5] The torsional angle around the O – O bond is slightly more then 50° giving additional evidence for rejecting the C_s model.

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Received April 19, 1969.