The molecular structure of gaseous 1,4-dioxane: An electron-diffraction reinvestigation aided by theoretical calculations

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HIGHLIGHTS

- Our structure results for dioxane are both more complete and more accurate than before.
- Our results are consistent with the theoretical prediction of only a chair form for the molecule.
- The distances, bond-, torsion-, and flap angles are similar to those in other ether-like molecules.

ABSTRACT

The structure of the molecule 1,4-dioxane (DIOX) has some features in common with other ring systems previously studied in this laboratory. In contrast to 1,4-cyclohexanedione, however, which consists both of a twisted boat form of D_2 symmetry and a chair form of C_{2h} symmetry, DIOX was reported, in two much earlier studies, to exist only as the chair form. The results of our work are in agreement with the earlier conclusions that gaseous DIOX exists either entirely, or essentially entirely (less than a few percent) in the chair form. Our work is much more extensive than the previous studies, and, aided by high-level theoretical molecular orbital- and normal-coordinate calculations, yielded the following bond distances (r_g/Å) and bond angles ($\angle_\alpha$/deg). $\langle C-H \rangle = 1.104$ (4), $C-O = 1.420$ (2), $C-C = 1.514$ (4), $\langle C-C-H \rangle = 105.4$ (55), $H-C-H = 108.0$ (26), $C-C-O = 111.1$ (3), $C-O-C = 110.9$ (10). The "flap" angle — the angle by which the COC plane is tilted up from the plane of the four carbon atoms — is equal to 50.6 (7)°. The structure is discussed and compared with the previous work and with predictions from theory.

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Introduction

The molecule 1,4-dioxane (DIOX) may be regarded as similar to that of 1,4-cyclohexanedione (CHDO) in that the carbonyl groups of the latter are replaced by oxygen atoms to generate the former. Since the ring bonds are in each case formal single bonds, it seems possible that in the gas phase the molecules would have similar structures. CHDO has recently been shown to exist as a mixture of the twisted boat and chair forms [1] in which the chair of C_{2h} symmetry is rigid and the twisted boat of D_2 symmetry is flexible. The nature of this flexibility is pseudorotation (internal rotations about bonds without angle strain). An important conclusion from the CHDO work was that the twisted boat form is the more stable, but that the vapor also contains about 23% chair.

There is an X-ray-diffraction investigation [2] of crystalline DIOX at 106 K in which the chair form (Fig. 1) was found. Also, two early investigations of this molecule by gas-phase electron diffraction [3,4] (GED) each detected only the chair form. Nevertheless, it seemed possible that in the gas phase the twisted boat form could be present in amounts too small to have been identified with the GED methods used by these early investigators many decades ago. For example, modern methods make use both of molecular orbital- and normal-coordinate calculations as an aid in the structure analysis, methods that lead to estimates of interatomic distances and amplitudes of vibration that cannot be experimentally measured. The theoretical approach was likely not available to the early investigators and the vibrational analysis appears not to have been done in either study.

We decided to reinvestigate the vapor-phase structure of DIOX as a part of some current research on organic ring systems. The main purpose was to expand the structural information available from the previous studies, neither of which included measurements of some of the parameters involving hydrogen atoms. The
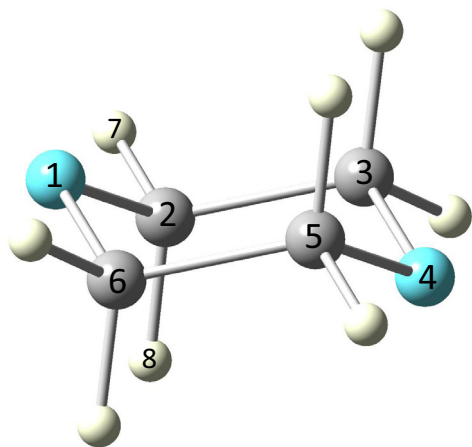

Fig. 1.

investigation would also provide a check on the values of the heavy-atom parameters and was expected to improve the precision of the parameter measurements.

Theoretical calculations

Molecular-orbital predictions of the structure and energy of the chair form of DIOX were carried out with the program Gaussian 03 [5] at several levels of theory and basis sets. The matter of the possible presence of a twisted-boat form quickly turned out to be a non-question: all calculations predicted this form to be of such high energy relative to the chair that its amount could be taken as negligible. The optimized energies from the B3LYP calculation can be seen in Table 1.

Since results from B3LYP theory had been used in the CHDO analysis, this theory was deemed appropriate for the current project on DIOX. The calculation also yielded Cartesian force constants which were used in the program ASYM40 [6,7] to calculate a number of quantities useful as constraints in the experimental structure analysis: in particular, vibrational amplitudes and conversion terms that relate the various distance types (r_α, r_g, and r_a).

Experimental section

The commercial sample of DIOX (Alfa Æsar, 99 + percent) was used as received. The diffraction experiments were made with the Oregon State University apparatus at a nozzle-tip temperature of 21 °C. Three diffraction photographs from the long camera distance (LC, 747 mm) and three at the middle camera distance (MC, 299 mm) were selected for analysis. Data concerning the experiments are the following. Film: Kodak electron image; development: 10 min in Kodak D-19 diluted 1:1; nominal accelerating voltage: 60 kV; electron-beam currents: 0.57–0.73 µA; sector
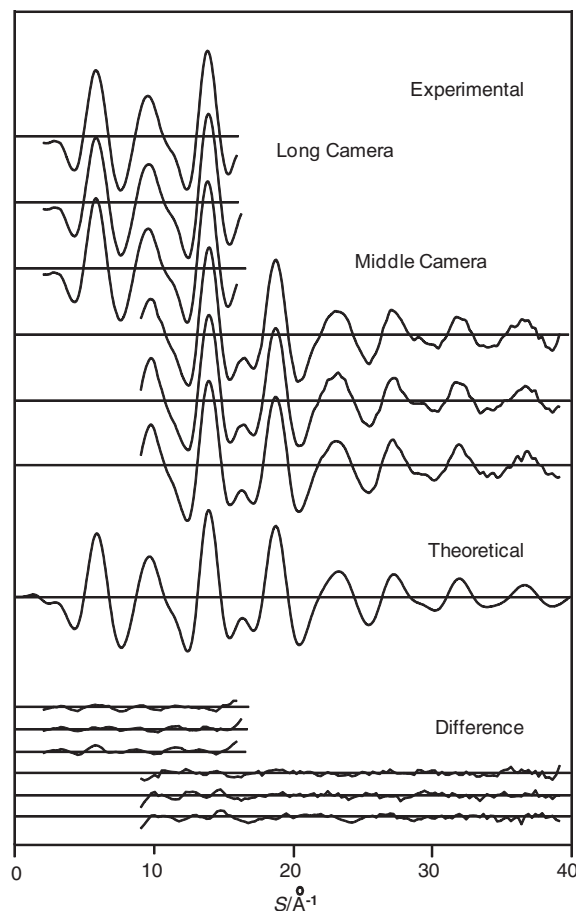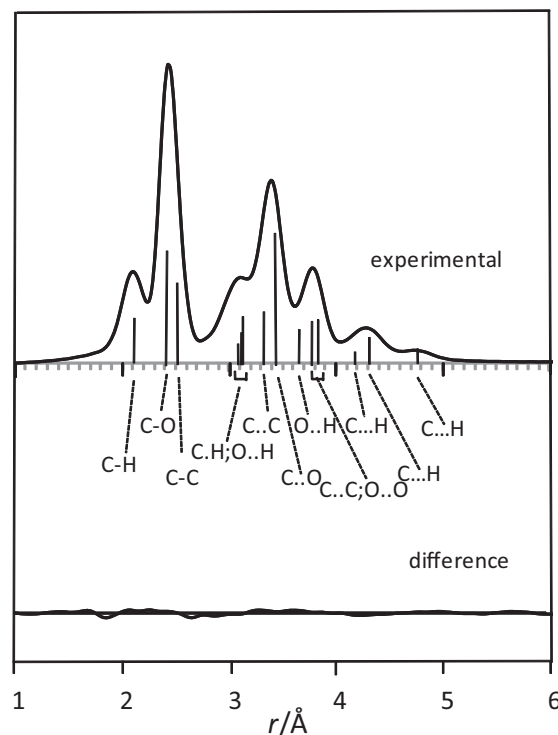
Table 1
Theoretical (B3LYP/cc-pVTZ) thermochemical data[a] for forms of 1,4-dioxane.

	Symmetry	$\angle$(OCCO)/deg	E^0	G^0	$m.f.$[b]
Chair	C_{2h}	56.6	0	0	~1.0
Twisted boat	D_2	60.7	6.3	6.0	$<10^{-4}$
Boat	C_{2v}	0	8.3	ts[c]	

[a] In kcal/mol at 298 K.
[b] Estimated mole fraction.
[c] Transition state.

Fig. 2.

Fig. 3.