Anomeric Effect and Charge Density of Dioxane and Dichlorodioxane *

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The low-temperature molecular structure and electron density (ED) distribution of dioxane and trans-2,5-dichloro-1,4-dioxane were determined near 100 K from X-ray data. Deformation electron density maps were calculated by Fourier and multipole expansion techniques. The multipole model charge distribution of dioxane determined from experimental data was taken as a reference state, relative to which the ED of the substituted ring was analyzed. These fragment deformation density maps show quadrupolar deformations on atoms O, Cl, and anomeric C only. The highly correlated orientation of the lobes at these atomic sites seems to indicate that the observed charge rearrangement is caused by three-center interactions.

Key words: Anomeric effect; Dichloro dioxane; Deformation electron density; Three-center interactions.

Trans-2,5-dichloro-1,4-dioxane crystals, structure from Altona et al. [1], and 1,4-dioxane, structure from Buschmann et al. [2], crystallized in situ in the cold gas stream of the diffractiometer, were used to collect the Bragg reflection X-ray and in the first case neutron data at a temperature of 100 K.

The phenomenon that electronegative substituents at the anomeric carbon of sugar rings prefer the axial setting, although by steric considerations the equatorial conformation would be favored, is called the anomeric effect, see Kirby [3]. It also influences the bond parameters. The geometry of this chlorinated molecule is in accord with the predictions of the effect. Deformation electron density maps were calculated by Fourier and multipole expansion techniques and compared to those obtained by ab-initio Hartree-Fock methods. The multipole-model charge distribution of dioxane determined from experimental data was taken as a reference state relative to which the electron density of the substituted ring was analyzed. On these fragment deformation density maps quadrupolar deformations were found at the sites of atoms O, Cl, and anomeric C (Fig. 1). The correlated orientation of the lobes at these three atoms may indicate that the observed charge rearrangement is due to three-center MO interaction in which all non-bonded

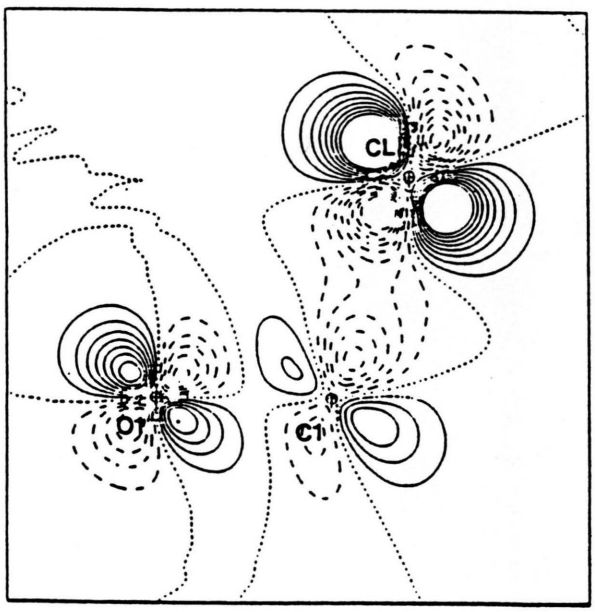

Fig. 1. Fragment deformation electron density in the O–C–Cl plane of dichlorodioxane with lobes of parallel orientation showing up; contour interval 0.1 e/Å^3.

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orbitals are involved. These maps show mixing of lone-pair orbitals at both ends of the O–C–Cl skeleton. The observed charge shifts at the terminal atoms seem to be more complex than what could be directly attributed to the interaction of partially occupied non-bonded with anti-bonding MOs. The observed rearrangement cannot be attributed to a π back-bonding, which is supposed to account for the anomeric effect and which may have only a secondary effect on the charge density. Ab-initio theoretical maps calculated with the help of the program Gaussian 86 [4] at the 6-31G* level did not reproduce these subtle findings. – This investigation will be published in detail [5].

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