**Short Communication**

**Dioxolanones and Related Compounds. II. The Molecular Structure of Methylene Oxalate Studied by Quantum Chemical Calculations**

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Methylene oxalate, the simplest carboxylic diester, was described for the first time in 1969, and was later studied by physical methods. The infrared and Raman spectra suggested a planar heavy-atom structure, point group $C_{2v}$. A structure deviating slightly from planarity was indicated by X-ray crystallographic data.

In the present work, the symmetry group and equilibrium geometry were determined by the semi-empirical MNDO method, which has been widely used in geometry optimization of relatively large organic molecules. The electronic structure was calculated for the MNDO equilibrium geometry by use of the Gaussian 80 *ab initio* program of Pople and coworkers.

**Point group.** With an initial geometry of $C_{2v}$ symmetry, and under its symmetry restrictions, an energy minimum was reached in the full optimization calculations. With an initial geometry of $C_{1}$ symmetry, obtained by distorting the $C_{2v}$-optimized geometry, full optimization led to the same heavy-atom structure as that obtained by optimization of the $C_{2}$ geometry. Methylene oxalate is thus predicted to belong to the point group $C_{2v}$ rather than to $C_{1}$ or $C_{2}$, in agreement with the infrared and Raman data.

**Equilibrium geometry.** As a final result of the MNDO optimization calculations, the parameter values for the equilibrium geometry shown in Fig. 1 were obtained. The angles are in relatively good agreement with the X-ray crystallographic data, but the experimentally observed bond distances are all somewhat shorter than ours, probably partly due to the large thermal motion of the atoms in the crystal. The calculated values for

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*Prof. Børge Bak et al. at the University of Copenhagen, Denmark, have recorded, but not yet published, the microwave spectrum.

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**Fig. 1.** Bond distances (Å) and bond angles (°) in the optimized geometry of methylene oxalate.

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bond angles and distances in C₂–C₆(O₂)–O₇–C₇ are not much different from the experimental values of the corresponding parameters in the general ester molecule (RCOOR'), and the local geometry around C₆ indicates typical sp³ hybridization, suggesting that there is no large ring strain.

The electronic structure was obtained by ab initio STO-3G calculations for the MNDO-optimized equilibrium geometry. Mulliken population analysis predicted that the charges located on the atoms O₁, O₃, C₁, C₇ and H₁ are −0.254, −0.202, +0.298, +0.141 and +0.09 e, respectively. The 26 occupied molecular orbitals were transformed into 26 localized molecular orbitals (LMOs) by the procedure of Foster and Boys. There are seven one-centred LMOs involving 1s orbitals on the heavy atoms. Of the remaining 19 LMOs, two one-centred LMOs on each of the oxygen atoms, one two-centred LMO in each of the H₁–C₁, H₂–C₁, O₁–C₇, O₂–C₇, O₇–C₁, O₈–C₂ and C₁–C₂ bonds, and two two-centred LMOs in each of the C₆–C₇ and C₆–O₇ bonds were found, which clearly indicate the lone pairs, single bonds and double bonds, respectively.

A heat of formation of −151 kcal mol⁻¹ and an ionization potential of 11.7 eV were predicted by the MNDO calculations.

References


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