Short Communication

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

De Mian Chen,[a,§] Ming Bao Huang[a] and Klaus Serck-Hanssen[b]

[a]Department of Modern Chemistry, University of Science and Technology of China, Hefei, Anhui, The People's Republic of China and [b]Department of Physiological Botany, University of Uppsala, P.O. Box 540, S-751 21 Uppsala, Sweden

Methylene oxalate, the simplest carboxylic diester, was described for the first time in 1969,[1] and was later studied by physical methods.[2,3,+] The infrared and Raman spectra suggested a planar heavy-atom structure, point group C_{2v}.[2] A structure deviating slightly from planarity was indicated by X-ray crystallographic data.[3]

In the present work, the symmetry group and equilibrium geometry were determined by the semi-empirical MNDO method,[4] which has been widely used in geometry optimization of relatively large organic molecules.[5,6,7] The electronic structure was calculated for the MNDO equilibrium geometry by use of the Gaussian 80 *ab initio* program of Pople and coworkers.[8]

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_s 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_s or C_2, in agreement with the infrared and Raman data.[2]

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,[3] 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.[3] The calculated values for
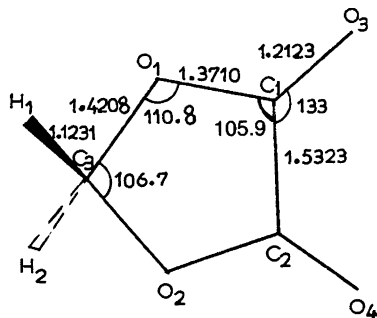

Fig. 1. Bond distances (Å) and bond angles (°) in the optimized geometry of methylene oxalate.

---

*For part I, see Ref. 1.
§To whom correspondence should be addressed.
+Prof. Børge Bak *et al.* at the University of Copenhagen, Denmark, have recorded, but not yet published, the microwave spectrum.

bond angles and distances in C_2–$C_1(O_3)$–O_1–C_3 are not much different from the experimental values of the corresponding parameters in the general ester molecule (RCOOR'), and the local geometry around C_3 indicates typical sp^3 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 O_1, O_3, C_1, C_3 and H_1 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.[9] 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 H_1–C_3, H_2–C_3, O_1–C_3, O_2–C_3, O_1–C_1, O_2–C_2 and C_1–C_2 bonds, and two two-centred LMOs in each of the C_1–C_3 and C_2–O_4 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

1. Serck-Hanssen, K. *Acta Chem. Scand. 23* (1969) 2900.
2. Fortunato, B. and Fini, G. *Spectrochim. Acta, Part A 31* (1975) 1233.
3. Kvick, Å. and Liminga, R. *Acta Crystallogr., Sect. B 36* (1980) 734.
4. Dewar, M. J. S. and Thiel, W. *J. Am. Chem. Soc. 99* (1977) 4899; *Ibid.* 4907.
5. Haddon, R. C. *J. Org. Chem. 44* (1979) 3608.
6. (a) Huang, M. B., Goscinski, O., Jonsäll, G. and Ahlberg, P. *J. Chem. Soc., Perkin Trans. 2* (1983) 305; (b) *Ibid.* (1984) 1327.
7. Huang, M. B. and Pan, D. K. *J. Mol. Struct.* (THEOCHEM) *108* (1984) 49.
8. Binkley, J. S., Whiteside, R. A., Krishnan, R., Seeger, R., Defrees, D. J., Schlegel, H. B., Topiol, S., Kahn, L. R. and Pople, J. A. *Q.C.P.E. 13* (1981) 406.
9. Foster, J. M. and Boys, S. F. *Rev. Mod. Phys. 32* (1960) 300.