The Use of Quantum-Chemical Semiempirical Methods to Calculate the Lattice Energies of Organic Molecular Crystals. Part II: The Lattice Energies of α- and β-Oxalic Acid $(COOH)_2$

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The lattice energies (ΔE_{lat}) of α- and β-oxalic acid ($(COOH)_2$) have been calculated using a recently introduced semiempirical quantum-chemical procedure. Within the framework of this method the lattice energy (ΔE_{lat}) is evaluated as the sum of the semiempirically calculated intermolecular dispersion (ΔE_{dis}), induction (ΔE_{ind}), repulsion (ΔE_{rep}), and electrostatic energy (ΔE_{els}). The lattice energies of the two polymorphs of oxalic acid obtained in this way correlate not only with the results of other calculations but also with the experimentally determined heats of sublimation in that the α-modification, which has a somewhat higher heat of sublimation, is slightly more stable than the β-polymorph. However, additional quantum-chemical calculations at the non-empirical *ab initio* level (e. g. ZPE+MP2(FC)/6-311++G**//MP2(FC)/6-311++G**) revealed that the absolute values of the lattice energies and the heats of sublimation are not directly comparable to each other because the structures of the $(COOH)_2$ molecules in the crystal lattices of both polymorphs differ significantly from that of the most stable form of the free molecule in the gasphase. At about 4.3 kcal/mol the calculated energy difference between the structure of the molecule in the solid state and the energetically most favourable conformation of the free $(COOH)_2$ molecule in the gasphase is much smaller than that in the recently described case of α-glycine (28 ± 2 kcal/mol). However, even such a small difference might be the source of serious problems if the heats of sublimation are employed to fit parameters to be used in the optimization of crystal packings.

Key words: Lattice Energies; Oxalic Acid; Calculations; Semiempirical Methods.