The Energetics of Hydrogen-Bonded Proton Exchange in Terephthalic Acid

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In a recent experimental solid-state NMR study, an experimental value for the energy associated with proton exchange in crystalline terephthalic acid was measured. We describe the application of existing computational methods, based on molecular mechanics, to calculate this energy. A preliminary calculation gives a value consistent with that determined experimentally. © 1989 Academic Press, Inc.

Recently, an NMR study of hydrogen-bonded proton exchange in terephthalic acid (see Fig. 1) has yielded a value of 1.8 ± 0.5 kJ/mole for the free energy of transition (*1*). The difference in energy between the two forms was attributed to "lattice effects in the crystalline solid." Here we report a preliminary attempt to use molecular mechanics to simulate these lattice effects.

The method assumes that the free energy of transition may be equated with the difference in lattice energy between two structures: a perfect, repeating crystal lattice and the similar structure in which only one of the proton pairs has exchanged (see Fig. 1). Changes in entropy and intramolecular energy are ignored, as are effects due to lattice relaxation. Lattice energies were calculated using the force field, atomic parameters, and partial charges derived by Lifson *et al.* (*2*) for carboxylic acids. The calculations were performed using a modification of the PCLEMC program (*3*), capa-

ble of calculating the lattice energy of a crystal structure containing one guest molecule. The transition actually involves two molecules (see Fig. 1); therefore, it was not possible to obtain the transition energy directly, and the calculation was carried out in three steps:

1. The lattice energy of the untransformed (perfect) structure was calculated, using available atomic coordinates (*4*), at a radius of 15 Å. Seventy-eight molecules were included, giving a lattice energy of −138.2 kJ/mole.

2. The lattice energy of a structure containing one guest molecule was calculated. The new coordinates (Table I) of the shifted carboxyl proton were generated by assuming that the new O–H bond was parallel to, and the same length as, the one it replaced. The atom types of the two oxygens were interchanged, but the coordinates were not altered. A value of +149.1 kJ/mole was obtained. This unrealistic value may be explained with reference to Fig. 2a. The proton in molecule 1 has been shifted, but that

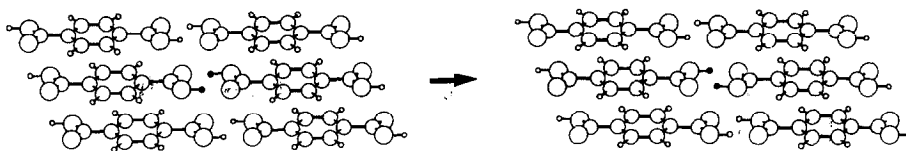* To whom correspondence should be addressed.

Fig. 1. Proton exchange in terephthalic acid. The transforming protons are black.

in molecule 2 has not. Therefore the interaction energy between these two molecules is large and positive. Removing this interaction energy from the total leaves an incomplete lattice energy of -106.4 kJ/mole.

3. To complete the calculation, two models were tried to calculate the correct interaction energy between molecules 1 and 2. In the first model the interaction was assumed to be the same as in the untransformed structure (Fig. 2b). For the second model, which corresponds most closely to the actual transition (Fig. 1), the positions of both protons in the carboxylic dimer

TABLE I

New Proton Coordinates

	X	Y	Z
Old	+0.5746	+0.3752	+0.1775
New	+0.3794	+0.5776	-0.1741

TABLE II

Lattice Energy Calculation

	First model (kJ/mole)	Second model (kJ/mole)
Incomplete lattice energy	-106.4	-106.4
$A-B$ interaction energy	- 30.9	- 31.6
Total lattice energy	-137.3	-138.0
Lattice energy, before transition	-138.2	-138.2
Change, per mole of molecules	+ 0.9	+ 0.2
Change, per mole of transition	+ 1.8	+ 0.4

were switched (Fig. 2c). The resulting interaction energies were added to the incomplete lattice energy calculated above, and the transition energy was deduced as shown in Table II. Note that lattice energies have been calculated per mole of molecules, whereas the experimental transition energy is per mole of transformation, i.e., per 2 moles of molecules.

Surprisingly, the first model gives good agreement with the experimental value of 1.8 ± 0.5 kJ/mole, whereas the second model gives too low an energy change. The difference arises predominantly because the intermolecular proton–proton distances in the second model are greater. The proton–proton interactions, which are calcu-
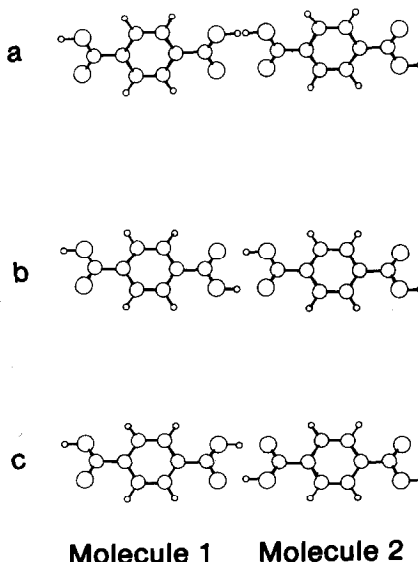

Molecule 1   Molecule 2

Fig. 2. The interaction between molecules 1 and 2.

lated to be entirely electrostatic, will in practice be heavily screened by the intervening atoms. Hence they will have been overestimated by this force field, which uses a constant relative permittivity of 2.

These preliminary calculations show that it is possible to simulate lattice effects in terephthalic acid. This study has only considered one transition in a system containing 78 molecules. A fuller investigation could consider different force fields and more concentrated systems, as well as the possibility that intramolecular energies alter in this transition.

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