MODELING THE CRYSTAL STRUCTURE AND ISOMERIZATION OF BENZOTRIFUROXAN

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Abstract: Using the methods of modeling the crystal structure in the atom–atom potentials approximation, the packing of benzotrifuroxan (C3h) and its isomer (Cs) as well as a hybrid crystalline form containing both molecules simultaneously are modeled. The simulation results are in good agreement with the available experimental data. It has been shown that the thermodynamically most favorable is the crystalline form with the C3h symmetry, followed by the hybrid and least favorable isomer form with the Cs symmetry. Isomerization processes have been investigated by quantum-chemical methods and the possibility of both one- and two-stage isomerization processes has been determined.

Keywords: method of atom–atom potentials; molecular electrostatic potential; isomerization of benzofuroxans; crystal structure prediction; nitroso intermediates

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Figure Captions

Figure 1 Structures of BTF (**1**) and its isomer (**2**) molecules

Figure 2 Experimental [3] (*a*) and calculated (*b*) crystal packings of compound **2** in the projection of unit cell from the side [101]

Figure 3 Calculated crystal packings: (*a*) compound **2**; and (*b*) hybrid phase (**1** + **2**). The groups undergoing isomerization are marked by the ovals. The unit cell projection is from the [101] side

Figure 4 Possible isomerization mechanisms of compound **2**

Table Captions

Table 1 Calculated and experimental unit cell parameters of compound **1**

Table 2 Calculated and experimental unit cell parameters of isomer molecule **2**

Table 3 The calculated and experimental parameters of crystal unit cell after the isomerization reaction of compound **2**

Table 4 Relative energies of benzotrifuroxan isomers with symmetry BTF (Cs) and BTF (C3h), dinitroso intermediate DNI (A), transition states of TS (1A), TS (2A) and TS (B), and elementary stages activation barriers of two- and one-step pathways isomerization (A and B)

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