3D Printing Space-Filling Models of Organic Compounds

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Introduction

Molecular models are indispensable learning aids in chemistry. However, commercially available model sets are limited in two important respects. The first is that students may view a thin wood or plastic cylinder as the location of the electrons in a molecule. The second is that the polygons typically used to represent atoms in student model sets are too small for students to understand when steric interactions between nonbonded atoms become significant.

3D printing is becoming recognized as a way to create entirely new physical models to enhance the teaching of chemistry. Recently we introduced 3D models of potential energy surfaces to teach conformational analysis and the energetics of competitive reaction pathways,[1,2] 3D models of P–V_m–T relationships to teach fundamental thermodynamic concepts,[3] and 3D models of structures with calculated geometries and p orbital isosurfaces.[4] Now we have developed methods to print two types of space-filling molecular models that can give students a better grasp of molecular electron density and steric interactions.

3D Printing Electron Density Surfaces

The space occupied by the electron density of a molecule is represented as a three-dimensional surface enclosing a specific percentage of its total electron density. That surface is termed an isosurface (isodensity surface), because points on the surface represent locations with identical local electron density. Including a greater percentage of electron density produces not only a larger 3D surface but also a somewhat different shape. For example, Figure 1 shows two electron density isosurfaces calculated for *tert*-butyl bromide. The surface on the left is defined by points at which the local electron density is 0.001 au (electrons/bohr^3), and that surface encloses 99.6% of the total electron density. The surface on the right indicates points with a local density of 0.01 au, and it encloses 96.9% of the total electron density.

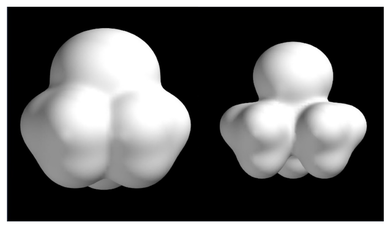

Figure 1. Calculated electron density surfaces for *tert*-butyl bromide.

We produced 3D models of calculated electron density surfaces through a process involving several steps. DFT calculations in *Spartan '16* provided the optimized geometry of a structure and isosurface values for different electron density values. An isosurface data set was pasted into *Excel*, from which a text file of *x,y,z* data points was saved as a text file. The data were then converted to a stereolithography (.stl) file with *MeshLab*.[5,6] *Meshmixer* and *netfabb Basic* were used to correct errors and to adjust the size of the model.[7,8] 3D prints were prepared using polylactic acid (PLA) filament and a Makerbot Replicator 2 printer. Figure 2 shows 3D models of the 0.002 au electron density isosurfaces of methyl bromide, ethyl bromide, isopropyl bromide, and *tert*-butyl bromide (clockwise from top left).

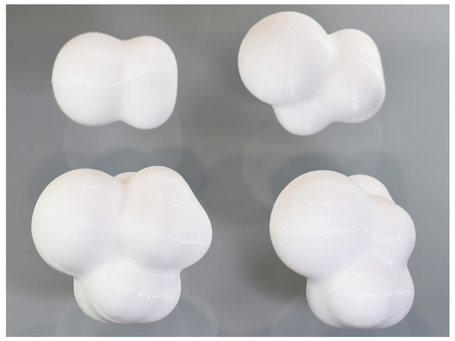

Figure 2. 3D printed models of alkyl halide electron density surfaces

3D Printing Models with van der Waals Radii

3D electron density surface models help students gain a new perspective on molecular structure and bonding. These models can also be used to study intermolecular steric interactions, but they have an important limitation. Students must infer nuclei locations from the shape of the model because electron density models do not provide color coding to help beginning students correlate the models to their commercial molecular model sets. Therefore we also developed space-filling models in which atoms are represented by spheres with sizes that are proportional to van der Waals radii.

To prepare such models, the optimized geometry of a structure was saved as a Protein Data Bank (.pdb) file. That file was opened in *VMD*,[9] from which its van der Waals representation was rendered as an .stl file.[10] Again, *netfabb Basic* and *Meshmixer* were used to check the .stl file for errors and to adjust the model size. The .stl files were printed as above and then painted in the usual atom colors (white for H, black for C, red for O, and dark red for Br). Figure 3 shows the resulting models for two alkoxide ions and four alkyl bromides.

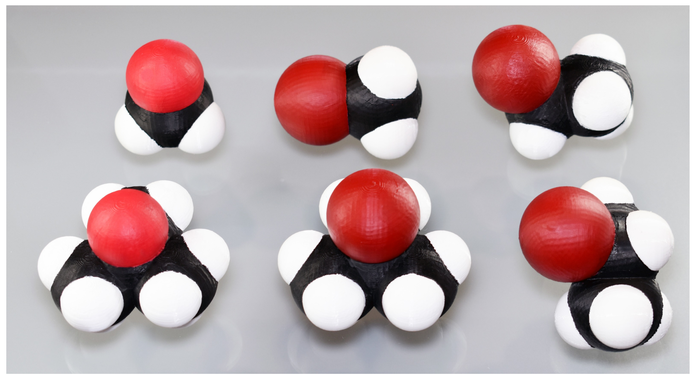

Figure 3. van der Waals models of (clockwise from top left) methoxide, methyl bromide, ethyl bromide, isopropyl bromide, *tert*-butyl bromide, and *tert*-butoxide.

Results

Students in first-semester organic chemistry courses used these models during short segments of regular laboratory periods. The electron density surface models helped them view a molecule as a region of electron density and not just as a set of nuclei held together by thin bonds. The painted van der Waals models were more helpful for studying bimolecular reactions, however.

Figure 4 shows the approach of methoxide to the back side of the α carbon of ethyl bromide (left) and the steric barrier to substitution when methoxide approaches the back side of the α carbon of *tert*-butyl bromide (right). By comparing the approach of the methoxide oxygen to the α carbon in all four of the alkyl bromides, students felt a physical sensation of the effects of increasing steric hindrance on S_N2 reactions. Furthermore, the models impressed on students the increasing opportunity for E2 reaction as a greater number of methyl groups both blocked the α carbon and increased the number of ß hydrogen atoms available for bimolecular elimination.

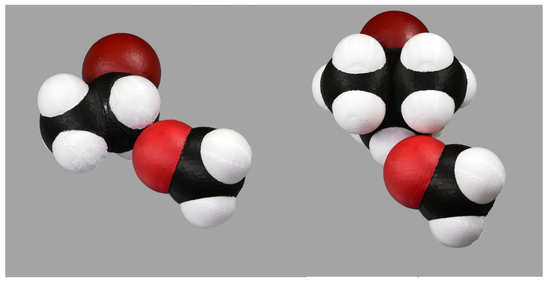

Figure 4. Approach of methoxide ion to the α carbon of ethyl bromide (left) and steric barrier to approach of *tert*-butyl bromide (right).

Conclusions

The space-filling 3D models provide students with kinesthetic learning activities that have been shown to provide persistent educational benefit, and our students found them helpful.[11,12] The procedures developed to produce these models can be extended to other space-filling models.

References

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