

ELECTRONIC SUPPORTING INFORMATION

Halogen derivatives of toluene under high pressure

*Szymon Sutula, Roman Gajda, Krzysztof Woźniak**

Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Żwirki i Wigury 101, 02-089 Warszawa, Poland.

DFT calculations in CRYSTAL14. DFT calculations to obtain the Equation of State (EoS) for 4-fluorotoluene were conducted within the pressure range from 0.1 to 3 GPa. Energy optimization was performed with the use of range-separated hybrid functional LC-wPBESOL.¹ An additional dispersion correction was not included because of the existing parametrizations for weak forces in this type of functionals.² A full relaxation of atomic coordinates and unit cell parameters by means of analytical energy gradients was applied. The 6-31G** basis set was used for all elements. This particular basis set was chosen deliberately, because it was recently shown³ that, in comparison with some larger triple- ζ basis sets such as 6-311G** and pob-TZVP (in the case of similar small organic compound), computational cost is drastically lower for 6-31G** basis set and the quality of results is very similar.

4-chlorotoluene, polymorph β . Theoretically possible transformations of $P2_1/n$ (the β phase) unit cell to $P2_1/c$ (the α phase) give the unit cell with parameters significantly different than in the α phase and completely not comparable. After such transformation, the β angle is equal to *ca.* 53°, which is rather unexpected and is one of the reasons why the unconventional $P2_1/n$ cell setting was chosen.

4-fluorotoluene, space group.

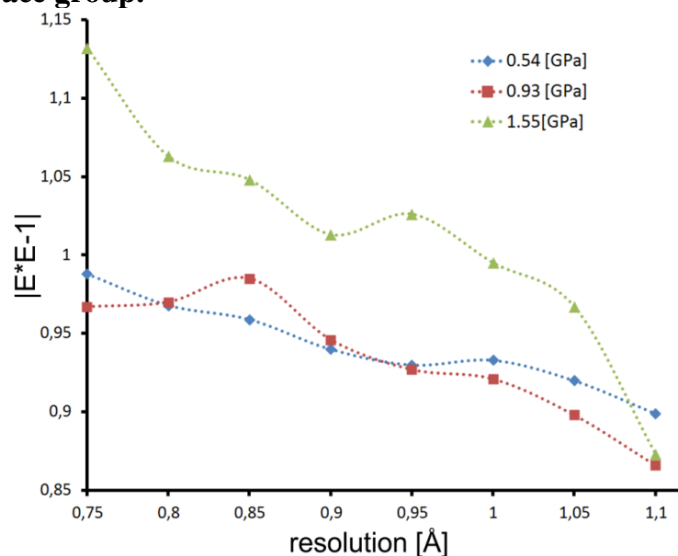


Figure 1. $|E^2-1|$ statistics as a function of resolution of the X-ray measurement.

Figure 1 presents calculations of $|E^2-1|$ statistics for the X-ray measurements of 4-fluorotoluene (conducted for three different pressures) as function of resolution. Although the $|E^2-1|$ factor is changing with the lowering resolution of measurement, it still corresponds to the centrosymmetric structure rather than the acentric one. This suggests that in the case of 4-fluorotoluene the $Pnma$ space group is a better choice than $Pna2_1$.

References

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