

Volume isotope effect in benzene; the anisotropic thermal expansion of H/D and halogen-substituted benzene crystals.

A.Dominic Fortes,^{1,*} and Silvia C. Capelli¹

¹ ISIS Facility, STFC Rutherford Appleton Laboratory, Harwell Science and Innovation Campus, Chilton, Didcot, Oxfordshire, OX11 0QX, U.K.

*(dominic.fortes@stfc.ac.uk)

Benzene is probably the most studied compound in the history of organic chemistry. This molecule may be considered the parent compound for most molecular crystals based on C–H $\cdots\pi$ interactions, and is therefore a valuable natural laboratory for evaluating the effect of tuning such interactions by, for example, atomic or isotopic substitution.

Lattice parameters of several benzene crystals have been measured using the High-Resolution Powder Diffractometer (HRPD) at the ISIS neutron spallation source. The protonated, deuterated and fluorinated benzenes, which are liquid at room temperature, were frozen by immersion in liquid nitrogen and then ground to a powder. The powders were transferred to chilled slab-geometry aluminium sample containers and then inserted into a CCR. Since C₆Br₆ is a solid at room temperature, this was loaded into a similar container under ambient conditions. The three low-melting-point analogues were measured up to within a few degrees of their melting temperatures; for C₆D₆, where pre-melting effects on the lattice parameters have previously been reported, data were collected in 2 K increments between 260 and 276 K. Hexabromobenzene was measured up to 360 K ($T/T_{\text{melt}} = 0.6$).

These datasets provide the first thermal expansion measurements on C₆F₆ and C₆Br₆. All of the benzene derivatives exhibit anisotropic expansion, but that of C₆F₆ is extreme. The expansion along the 2-fold axis is several times larger than the greatest linear expansion in any of the other analogues. Moreover, there is a dramatic variation in the linear expansion along the *c*-axis, with a substantial increase in expansivity above 200 K. This corresponds well with other experimental data indicating the onset of rotational disorder at this temperature.

The thermal expansion of the protonated and deuterated analogues of benzene are essentially identical (Fig. 1); as such, despite an absolute difference, the molar volumes of C₆H₆ and C₆D₆ as a function of temperature are parallel curves. This contrasts with the result of Dunitz and Ibberson (2008), also measured on HRPD, which showed the molar volumes crossing at ~ 170 K, that of deuterobenzene being larger at higher temperatures. Since our samples are heated *in situ* (using cartridge heaters inserted the frame of the sample holder) and we have allowed plenty of time for equilibration, we are confident of the accuracy of our sample temperatures. Furthermore, our C₆D₆ data are in excellent absolute agreement with Jeffrey *et al.* (1987) and Craven *et al.* (1993).

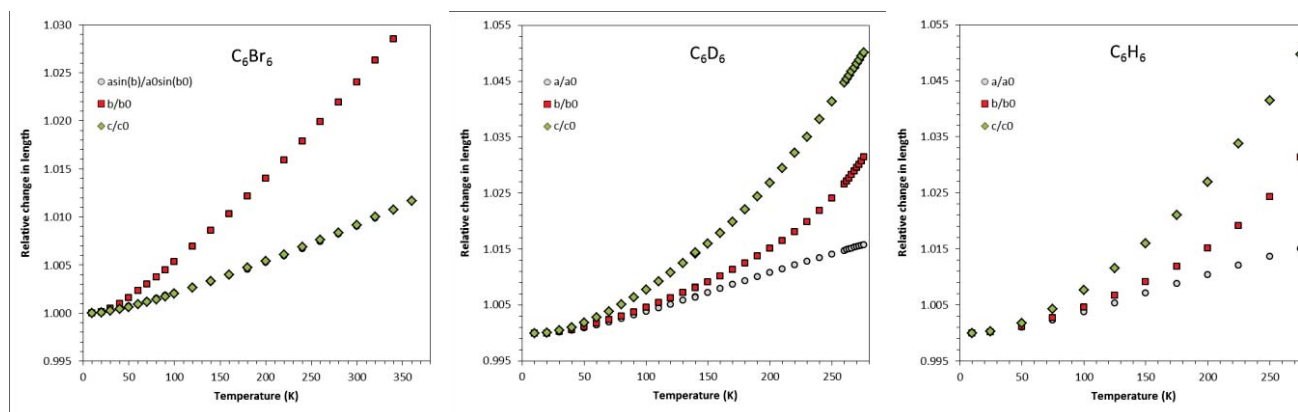


Figure 1: Relative change in length of a^* , b and c in C₆Br₆ (left) and of a , b and c in deuterated and protonated benzene (centre and right) as a function of temperature.

One striking preliminary results is that the relative change in unit-cell volumes, when normalised by the respective melting temperatures, are very similar for the low melting-point species C₆H₆, C₆D₆ and C₆F₆, whereas that of the higher melting-point species C₆Br₆ differs significantly.

References

Craven *et al.* (1993) *J. Chem. Phys.* **98**, 8236; Dunitz & Ibberson (2008) *Angew. Chem. Int. Ed.* **47**, 4208; Jeffrey *et al.* (2008) *Proc. Royal Soc. London A* **414**, 47.