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Prediction of the pressure-dependent polymorphism of benzene. By DAVID HALL,* THOMAS H. STARR,† DONALD E. WILLIAMS† AND MURRAY K. WOOD,* *Chemistry Department, University of Auckland, Auckland, New Zealand and Chemistry Department, University of Louisville, Louisville, Kentucky 40208, USA*

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Abstract

Calculation of the lattice energy and cell parameters of a crystal structure under pressure is discussed. This enables estimation of the enthalpy change for a high-pressure phase change.

Calculations of the lattice energy of hydrocarbon crystals have shown that the global energy minimum occurs very close (in parameter space) to the observed structure, and that this can be true for a surprisingly wide variation in the nonbonded potential parameters used (Ramachandran, 1974). The calculated value of the lattice energy is not so uncritical of the potential parameters, and when pressure-dependent polymorphism occurs, as with benzene, prediction that the correct phase is stable is a more severe test (Williams, 1974; Hall, Headford & Jarvie, 1978). The calculation of the lattice energy of benzene polymorphs under applied pressure has been discussed previously (Hall & Williams, 1975) but that discussion omitted consideration of a $P\Delta V$ term.

Under an applied pressure, a crystal contracts so that the repulsive intermolecular forces equal those applied,

$$dE = -PdV$$

and

$$\frac{\partial E}{\partial p} = \frac{-P\partial V}{\partial p},$$

where p is any parameter. For example, for a monoclinic crystal $\partial E/\partial a = Pbc \sin \beta = PV_{\text{cell}}/a$, and similarly for b and c . At atmospheric pressure these derivatives are not significantly different from zero, and the standard procedure for lattice-energy minimization targets them to zero (Kitaigorodsky, 1973). If the nonbonded potential parameters are correct, the calculated values of the derivatives should also be small at the observed structure, and only small unit-cell changes should be required to make them vanish.

At kilobar (100MPa) pressures the derivatives must be targetted to the correct nonzero value. The crystal under such high pressure can be expected to have a smaller unit-cell volume. In addition, there is the possibility of a phase transition to a different mode of molecular packing at high pressure. Such a phase transition occurs in solid benzene at 25 kbar pressure (Piermarini, Mighell, Weir & Block, 1969).

We have calculated the lattice energy and associated cell parameters for benzene I (Bacon, Curry & Wilson, 1964), and high-pressure benzene II for zero and 25 kbar pressure, using the program PCK6 (Williams, 1972, 1979) and the

potential parameters as described by Williams (1974). The results are in Table 1. It is apparent that the lattice energy is lower (more negative) for benzene I at both pressures, but that the molecular volume for benzene II is smaller. It is necessary to correct the results for the work $P\Delta V$ associated with this volume change. For the benzene I \rightarrow benzene II transition at 25 kbar, ΔU is $+0.75 \text{ kJ mol}^{-1}$, $P\Delta V$ is $-2.67 \text{ kJ mol}^{-1}$, and therefore the enthalpy change is $-1.91 \text{ kJ mol}^{-1}$. The benzene II structure is thus correctly predicted as the more stable at the high pressure.

Molecular-packing calculations enable both the change in lattice energy and the volume-expansion work contribution to the enthalpy change to be estimated, and thus permit the prediction of pressure-dependent phase changes, at least when, as with benzene, both phases are ordered. Future work should consider the entropy difference between polymorphs and determine if it can reasonably be neglected.

Table 1. *Lattice-energy minima for benzene crystal structures*

	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³ / molecule)	<i>E</i> (kJ mol ⁻¹)
Benzene I					
obs (1 bar)*	7.39	9.42	6.81	118.52	
calc (0 bar)	7.433	9.300	6.925	119.97	-54.25
calc (25 kbar)	6.989	9.003	6.467	101.73	-42.85
Benzene II					
obs (25 kbar)	5.417	5.376	7.532	103.06	
calc (0 bar)	5.694	5.516	7.957	117.42	-53.10
calc (25 kbar)	5.426	5.247	7.473	99.96	-42.09

* 1 bar = 0.1 MPa.

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