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ortho, meta, para isomers of dichlorobenzene, with melting points: ortho −17.5°C, meta −24.4°C, para +52.5°C

Figure 1: ortho, meta, para isomers of dichlorobenzene, with melting points: ortho −17.5°C, meta −24.4°C, para +52.5°C

Abstract

Full Text

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SYMMETRY OF A MOLECULE, MELTING OF A CRYSTAL, AND ORDERING OF A LIQUID

It is intuitively clear that more symmetric molecules should fit into a crystal lattice more easily, more conveniently, and more readily. One may expect that, other conditions being equal, the melting temperature of a crystal will be the higher, the greater the symmetry of the molecules composing it.

Having made certain assumptions about the thermal motion of molecules in the liquid phase, one can predict the expected influence of molecular symmetry on the melting temperature. At the same time, quantitative agreement between such a calculation and experiment cannot be expected, since when the symmetry of a molecule changes, its other properties also change, and these also affect the structure of the crystal, the packing density of the molecules, and the lattice energy. Nevertheless, it seems of interest to clarify the role of molecular symmetry as one of the factors influencing the conditions of melting.

For verification it is convenient to use isomeric organic molecules. As an example, let us consider disubstituted chlorobenzene, $C_6H_4Cl_2$, which has 3 isomers; the chlorine is indicated by bold dots, and the symmetry axes by dashed lines:

The para molecule is the most symmetric, and indeed the melting temperature of para-dichlorobenzene is higher than that of the ortho and meta compounds. Such a situation is characteristic of many organic molecules. It is clear that the indicated regularity does not exclude other rules (for example, differences in the melting temperatures of α- and β-derivatives of naphthalene, which have the same symmetry) associated with the influence of structure on the lattice energy.

For a theoretical explanation of the influence of symmetry we assume that in a crystal the molecules are regularly situated at the lattice sites and are correctly oriented relative to one another; the entropy of the crystal at 0°K is equal to zero.

In a liquid the positions of neighboring molecules are strongly correlated; the distances between neighboring molecules differ little from the distances in the crystal. However, there is apparently no mutual orientation of the molecules in the liquids under consideration. In other words, we assume that the so-called "short-range order" in a liquid pertains to the positions of the centers of the molecules, but not to the angles characterizing the orientation of the molecule in space; i.e., the interaction of molecules in a liquid substantially affects their translational motion, but affects the rotation of the molecules to a much lesser degree.

Such a situation corresponds to the commonplace notions: "in a solid body molecules vibrate, in a liquid they rotate, in a gas they rotate and undergo translational motion."

As is known, the rotational entropy of a molecule depends on its symmetry,

$S(T) = s(T) - R \ln n,$

where n is the so-called symmetry number of the molecule.

Indeed, the rotation (spatial orientation) of an arbitrary asymmetric body (molecule) is characterized by three Euler angles; for given values of the moments of inertia, the corresponding entropy per mole is equal to $s(T)$. However, if the molecule has certain symmetry elements, then in the space of the three Euler angles several (n) points correspond to physically indistinguishable orientations of the molecule; to characterize the orientation of the molecule one need not use the entire space of Euler angles, but only $1/n$ of it. Corresponding to the decrease in phase volume, the entropy also decreases.

The entropy of the crystal does not depend on the symmetry of the molecule.

Assuming that all the remaining properties of the molecule and of its thermal motion do not change appreciably when the symmetry changes, we obtain the expression for the total entropy of the liquid

$$S_l(T) = s_0(T) - R \ln n. \tag{1}$$

We shall also assume that the energy of the crystal and the energy of the liquid at a given temperature do not depend on the symmetry of the molecule.

The free energy of the crystal is

$$F_{\text{cr}}(T) = E_{\text{cr}}(T) - TS_{\text{cr}}(T). \tag{2}$$

The free energy of the liquid is

$$F_\mathrm{l}(T) = E_\mathrm{l}(T) - Ts_0(T) + RT \ln n. \tag{3}$$

The melting temperature is determined by the condition of equality of the free energies (taking the pressure to be small, we neglect the difference between the free energy and the chemical potential), whence we obtain in an elementary way

$$\Delta T = \frac{RT_\mathrm{m}^2}{Q_\mathrm{m}} \Delta \ln n, \tag{4}$$

where Q_m is the heat of melting.

In deriving the formula it is not assumed that the heat of melting is constant; owing to the different heat capacities of the crystal and the liquid, the change in T_m caused by the change in n, in turn, leads to a change in Q_m.

Let us compare expression (4) with experiment.

In the case of disubstituted benzenes with identical substituents, the symmetry number is, for the ortho and meta positions, $n = 2$, and for the para position $n = 4$.

For the dichlorobenzenes the heat of melting has been measured and is equal to 3.09 (o), 3.02 (m), 4.35 (p) kcal/mole; the melting temperatures are 255.5° (o), 248.5° (m), 325.5° (p).

The mean heat of melting is 3.5 kcal/mole, the mean melting temperature is 277° K; consequently, the expected difference of melting temperatures is

$$\Delta T = \frac{RT_\mathrm{m}^2}{Q_\mathrm{m}} (\ln 4 - \ln 2) = 30^\circ.$$

Experimentally,

$$\Delta T = T_\mathrm{para} - \frac{1}{2}(T_\mathrm{meta} + T_\mathrm{ortho}) = 73^\circ.$$

It follows from our assumptions that T_meta and T_ortho should be equal to one another; experimentally, $T_\mathrm{meta} - T_\mathrm{ortho} = -7^\circ$.

Thus, one can speak only of the correct sign and order of magnitude of the effect, which is not surprising in view of the extremely simplifying assumptions made about the sameness of the thermal functions of molecules of different structure.

It must be emphasized that the influence of the symmetry of the molecule on the entropy of the liquid does not imply free rotation of the molecule in the liquid; the molecule may execute rotational oscillations with rare by jumps from one orientation to another. It is only necessary that in the liquid the different orientations of the molecule be equally probable and practically independent of the orientation of neighboring molecules.

A weaker influence of symmetry,

$$\Delta T < \frac{RT^2}{Q} \Delta \ln n,$$

is possible in two cases:

1) When there is no complete ordering in the crystal. Such a case arises if the physical difference between the groups determining the symmetry of the molecule is small—for example, when hydrogen is replaced by deuterium; one may suppose that the melting temperatures of the isomers $C_6H_4D_2$ do not differ, since in the crystal D and H are not ordered. In this case the entropy of the crystal at 0°K is nonzero and also depends on the symmetry of the molecules.

2) When partial ordering of orientations is preserved in the liquid at the melting temperature. Such a case can in principle arise in the presence of large, strongly interacting substituent groups; however, no large effect can be expected here, since such groups raise the melting temperature of all isomers.

A stronger-than-calculated influence of symmetry in the case of disubstituted benzene means that, along with the entropic influence, there is also an influence of structure on the energy of the crystal and the liquid; the difference in the heat of fusion of the pair of dichlorobenzenes from that of the other isomers is apparently greater than $(c_\ell - c_k)\Delta T$.

A systematic investigation of various isomers, with measurement of heats of fusion and heat capacities of both phases and comparison of the influence of symmetry with direct X-ray studies of the ordering of molecular orientations in the liquid, is of interest.

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Note: Figure translations are in progress. See original paper for figures.

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