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CONDITIONS FOR THE FORMATION OF SOLID SOLUTIONS OF ORGANIC SUBSTANCES

(Presented by Academician A. N. Nesmeyanov, 16 X 1956)

The attractive forces acting between the molecules from which an organic crystal is built possess extremely weak directionality. Therefore the tendency toward minimum energy finds its expression in the tendency toward close packing (^{1}). The categories of symmetry and close packing prove entirely sufficient for understanding the structure of an organic crystal. In contrast to this, in metallic and inorganic crystals interatomic electronic bonds may completely suppress the factors of symmetry and close packing.

It is precisely for this reason that, for organic substances, one may attempt to formulate rules for the formation of solid solutions—an attempt that is unsuccessful for other classes of compounds. In organic crystals, substitutional solid solutions are chiefly possible. A foreign molecule is capable of replacing a molecule of the parent crystal if the molecules of both types are similar in shape and size.

Similarity of atomic dimensions in inorganic and metallic crystals is a necessary condition for the formation of substitutional solid solutions. In organic crystals, the condition of similarity in the shape and size of molecules is necessary and sufficient; here, however, it is considerably more difficult to characterize molecular isomorphism quantitatively.

Analysis of the available experimental data shows that substance A dissolves in substance B under the following condition. Let us imagine that one molecule of substance B has been removed from the crystal. Into the vacated place in the ideal lattice of crystal B we put molecule A. If the substitution can take place with approximately the same number of contacts and with the intermolecular radii preserved within permissible limits, then solid solutions are formed upon mixing. The permissible limits of the intermolecular radii of the atoms H, C, N, and O are, respectively, the values 1.05–1.35; 1.65–1.85; 1.45–1.65; and 1.30–1.50 Å.

In what follows, we shall attempt to establish a correlation between the solubility fraction and the dimensions of the compressions and voids arising upon mixing.

Dissolution by interstitial incorporation is possible in organic systems only in rare cases. The packing coefficients of organic molecules in a crystal lie within the range from 0.6 to 0.8 ([1]). This means that in organic crystals small voids are possible, with a total volume on the order of 10% of the volume of the molecule.

Thus, interstitial solid solutions of A in B are formed in the case when the molecules of A are approximately 10 times smaller in volume than the molecules of B. Of course, not only the volume but also the shape of the void is important.

Substitutional solid solutions of organic substances are also possible with unlimited solubility; however, for the formation of such solutions

isomorphism of molecules is only a necessary, but not a sufficient, condition.

If molecules A and B are close in size and shape, then molecules A can replace molecules B in the crystal. Upon substitution, the symmetry of the arrangement of molecules in crystal B may either remain the same, or change abruptly as soon as the first molecules A enter B.

The symmetry of the arrangement of molecules in crystal B must remain the same in the following cases: a) if molecule B occupies an asymmetric* position in the crystal, then for any symmetry of molecule A; b) if molecule B occupies a non-asymmetric position in the crystal, then for non-asymmetric molecules A, or in the presence of equal numbers of left- and right-handed forms of molecules A.

The symmetry of the arrangement of molecules in the crystal will change abruptly when the first molecules A enter the solution if molecule B occupies a non-asymmetric position in the crystal and molecules A are asymmetric (one of the forms).

Let A be soluble in B and B soluble in A. With similar molecular forms, a continuous series of solid solutions is possible in the following cases: a) if the symmetry of the arrangement of molecules in crystals A and B is the same; b) if the symmetry of the arrangement of molecules in crystals A and B differs, but the symmetry of the arrangement of molecules in crystal B changes abruptly when molecules A enter crystal B. This will occur in particular when asymmetric molecules dissolve in a racemate.

A continuous series of solid solutions is impossible if the symmetry of the arrangement of molecules in crystals A and B is different and, moreover, molecules A enter B without changing the symmetry of the arrangement of molecules in crystal B, while molecules B enter A without changing the symmetry of the arrangement of molecules in crystal A. In this case there are two solid phases, and hence a miscibility gap.

If we do not speak of asymmetric molecules, then it may be said that a necessary condition for the formation of solid solutions in all proportions (this applies to all three types of continuous solid solutions) is identical symmetry of the mutual arrangement of the molecules of the substances being mixed, i.e., identical space groups and numbers of molecules in the cell.

We know examples of organic substances in which not only are the molecules very close in shape and size, but the molecular packings are also very similar. If, with this closeness, there is nevertheless a difference in the symmetry of the mutual arrangement of molecules, then a continuous series of solid solutions becomes impossible. In some concentration interval there must be a miscibility gap or, in other words, a continuous change in concentration in the solid state is possible only through a phase transition.

The closer the molecules of such crystals are in shape and the more closely related their packings, the narrower the miscibility gap should be. It is therefore not surprising that investigators did not observe this gap and found a continuous series of solid solutions of types I and III where, in fact, solutions of types IV and V, respectively, occurred.

An exceedingly large number of systems have been described in the literature, incorrectly, as continuous solid solutions.

Thus, for example, the following systems have incorrectly been assigned to solid solutions of type I (data taken from Landolt): anthracene—carbazole; anthracene—phenanthrene; benzene—thiophene; heptadecane—hexadecane; heptadecane—octadecane; diphenyl—3-fluorodiphenyl; dibenzyl—stilbene; dibenzyl —tolane; naphthalene—β-naphthol.

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* An asymmetric position or body contains no center of inversion and no mirror planes of symmetry.

Erroneously assigned to type III were: acridine—anthracene; acridine—phenanthrene; azobenzene—dibenzyl; naphthalene—β-chloronaphthalene; 1,5-dinitronaphthalene—1,8-dinitronaphthalene; 1,5-dinitronaphthalene—1,3,8-trinitronaphthalene; diphenyl—2-fluorodiphenyl; diphenyl—3-fluorodiphenyl.

It is sufficient to note that anthracene, diphenyl, and naphthalene have 2 molecules in the crystal cell of symmetry C_{2h}^5, which is impossible for substances whose molecules lack a center of symmetry.

We encountered erroneous state diagrams in studying the structure of solid solutions of organic substances by the method of X-ray structural analysis. The results of this work, above all concerning the structure of solid solutions of the systems stilbene—dibenzyl and phenanthrene—anthracene, will be reported elsewhere.

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

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