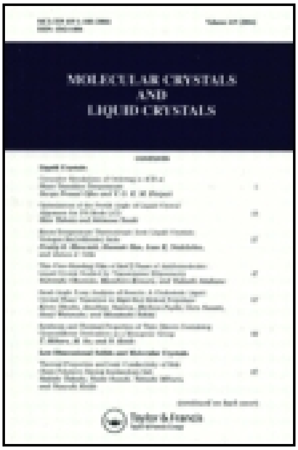

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Lattice Distortions in Organic Solid Solutions

R. M. Myasnikova [a]

[a] A. N. Nesmeyanov Institute of Elemento-Organic Compounds, The USSR Academy of Sciences, Vavilov Str. 28, Moscow, B-334, USSR

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Lattice Distortions in Organic Solid Solutions

R. M. MYASNIKOVA

A. N. Nesmeyanov Institute of Elemento-Organic Compounds, The USSR Academy of Sciences, Vavilov Str. 28, Moscow B-334, USSR

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X-ray diffraction measurements of lattice distortions in organic solid solutions are discussed within the framework of model ideas of organic chemical crystallography. The distortions are shown to have a complicated concentration dependence. In each particular case this dependence is governed by similarity in geometrical dimensions of the mixed molecules, by peculiarities of the molecular packing in the matrix crystal and by the way through which the guest molecules enter into the matrix.

The geometrical model of a molecular crystal serves as a first approximation model in organic crystal chemistry. Behind it is the representation of a structure as a close packing of molecules having definite shape and dimensions.[1] We successfully use this model to study binary organic systems, mainly, substitution solid solutions. A comparative analysis of molecular packing in the matrix crystal and in a solid solution is an illustrative and simple procedure, which is indispensable in interpreting the experimental results and revealing general regularities of formation of solid solutions. In some cases, however, such a model analysis turns out to be insufficient and a thorough X-ray diffraction study is called for.[2]

In the present paper, we attempt to use model packing principles for analyzing the lattice distortions occurring in organic solid substitutional solutions.

Crystallographic analysis of the structure of inorganic solid solutions, e.g. of metal alloys, is generally curried out using the data on the variation of the unit cell parameters with concentration, x. It is known that Vegard's law, according to which the variation of a lattice period with composition should be linear, is fulfilled in exceptionally rare cases. No more effective appears Söhn's law, which requires a linear variation for the unit cell volume.[3] The linear dependence of $a(x)$ or $V_{\text{cell}}(x)$ is rather an exception than a rule.

The formation of substitutional solid solutions by organic (molecular) substances is most commonly accompanied by distortions of the unit cell. The substitutional solid solutions of the inter-block type[2,4-6] are an exception and their discussion is beyond the scope of the present paper.

The overwhelming majority of organic crystals are of low symmetry. Therefore, the use of variations of the six parameters $a, b, c, \alpha, \beta, \gamma$ in the general case as a measure of distortions, occurring in a solid solution, is inconvenient, though it is indeed possible to explain these variations through a geometrical analysis of the molecular packing. It is reasonable to take $\tau(x) = V_{\text{cell}}(x)/Z$ as a single characteristic of lattice distortions. Here $V_{\text{cell}}(x)$ is the unit cell volume calculated from precise X-ray measurements of the unit cell edges and angles; the number of molecules in the cell is $Z(x) = Z(0) =$ constant for the substitutional solid solutions, $\tau(x)$ is thus the unit cell volume per "average" molecule in the substitutional solid solution crystal.

It is clear that for an organic solid solution the following linear dependence may be regarded as an analog of Zöhn's law:

$$\tau_l = (1 - x)\tau_A + x\tau_B = \tau_A + x(\tau_B - \tau_A).$$

Here τ_A and τ_B are the unit cell volumes per molecule in pure substances A and B, respectively.

An inspection of the results of single-crystal X-ray diffraction measurements[4-11] performed in this laboratory with a number of solid solutions,[12] and also of the data reported by other authors,[13-19] provides no example of additive variations of $\tau(x)$.

The known condition for formation of a substitutional solid solution is that the molecules of the substances to be mixed are close in shape and dimensions. This condition, however, is necessary but not sufficient. It is just for this reason that the parameter of molecular isomorphism, ϵ, introduced in our early study[1] has proved to be of little utility. The reason is that the decisive factor governing the formation of a solid solution is the structure of the matrix crystal, while the molecular isomorphism parameter is of minor importance. And it is the pattern of the molecular packing in the matrix crystal that determines "convenient" or "inconvenient" positions of the guest molecules in the substituted sites of the matrix lattice. This governs the character of distortion of the solid solution lattice and, ultimately, the limits of solubility in the solid state. Some examples are presented below.

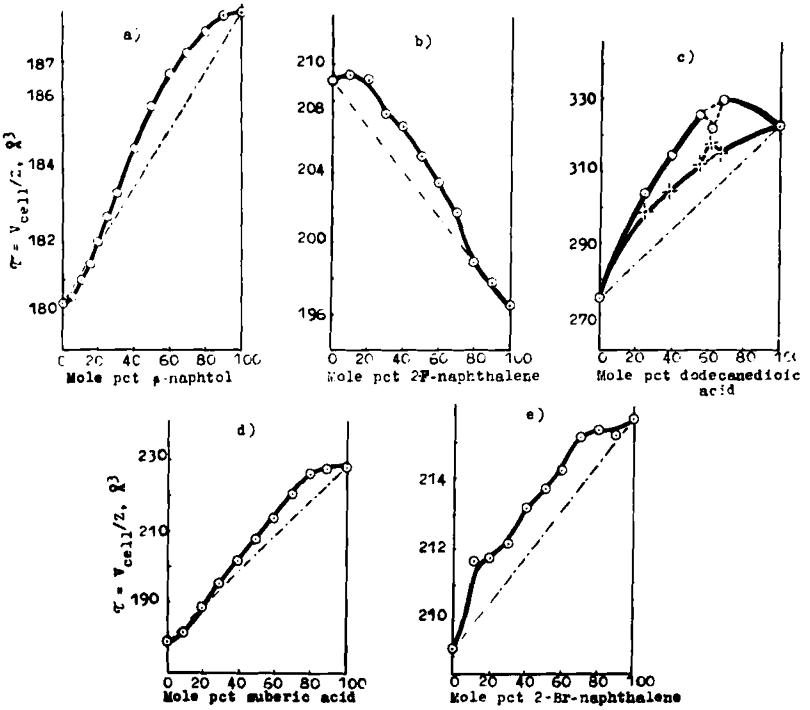

FIGURE 1 Concentration variations of specific volumes $\tau(x)$, in systems with a continuous series of solid solutions: (a) naphthalene–β-naphthol;[13] (b) 2-Cl-naphthalene-2-F-naphthalene;[15] (c) sebacic acid–dodecanedioic acid;[16] (d) adipinic acid–suberic acid;[17] (e) 2-Cl-naphthalene-2-Br-naphthalene.[19]

The curves in Figures 1–3 are plotted according to the data of X-ray measurements referred to in figure captions. Five examples in Figure 1 refer to systems forming continuous series of solid solutions. The two noncoinciding curves of $\tau(x)$ in Figure 1c correspond to two different methods of growing solid solution crystals: melting (⊙) and sublimation (><) of the component mixture.

For systems with limited solubility the dependences $\tau(x)$ are plotted up to the respective solubility limits. Figure 3a shows a system of the peritectic type; Figure 3d refers to a system with a complicated eutectic–peritectic diagram of state. The other examples in Figures 2 and 3 refer to systems of the most common eutectic type.

The dot-and-dash lines in all figures correspond to the additive variation of τ_i. The ordinate scale is chosen with allowance for the accuracy of X-ray measurements.

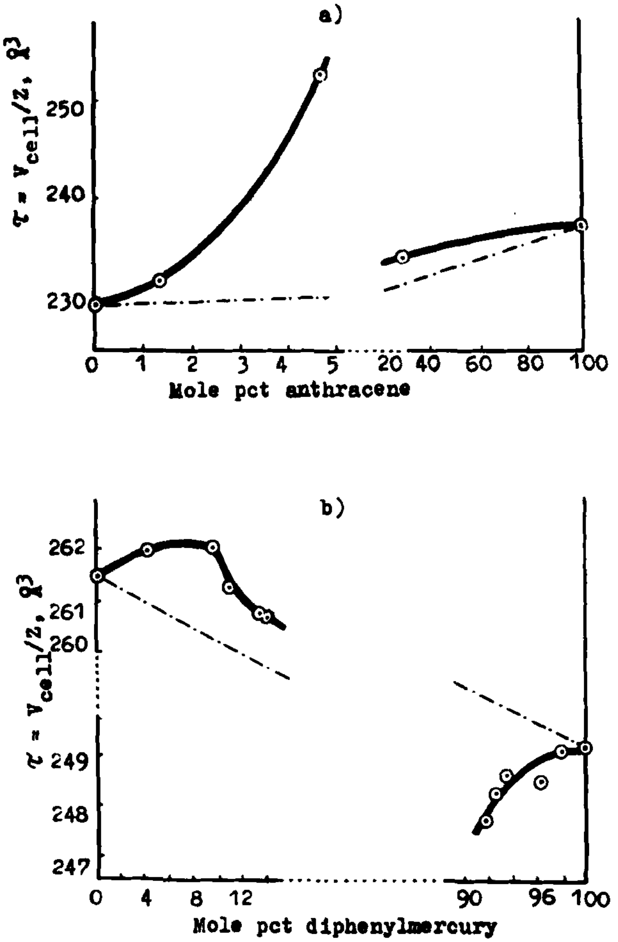

FIGURE 2 Variations of $\tau(x)$ in the systems with limited solubility: (a) acridine–anthracene;[8] (b) tolan–diphenylmercury.[10]

The asymmetric shape of the curve of the intermolecular interaction potential suggests that the retention of cavities in the solid solution is energetically more preferable than the formation of tightness around the guest molecules. In principle, one may expect that the curve $\tau(x)$ will be below the additive curve τ_l, if the guest molecule (G) is smaller than the matrix molecule (M), $V_G < V_M$, and it will be above τ_l for $V_G > V_M$. Some of the examples presented (Figure 1c,e, Figure 2a, Figure 3) can be well explained in terms of this simplified scheme. But to reveal all details of the lattice distortions in solid solutions, and to ex-

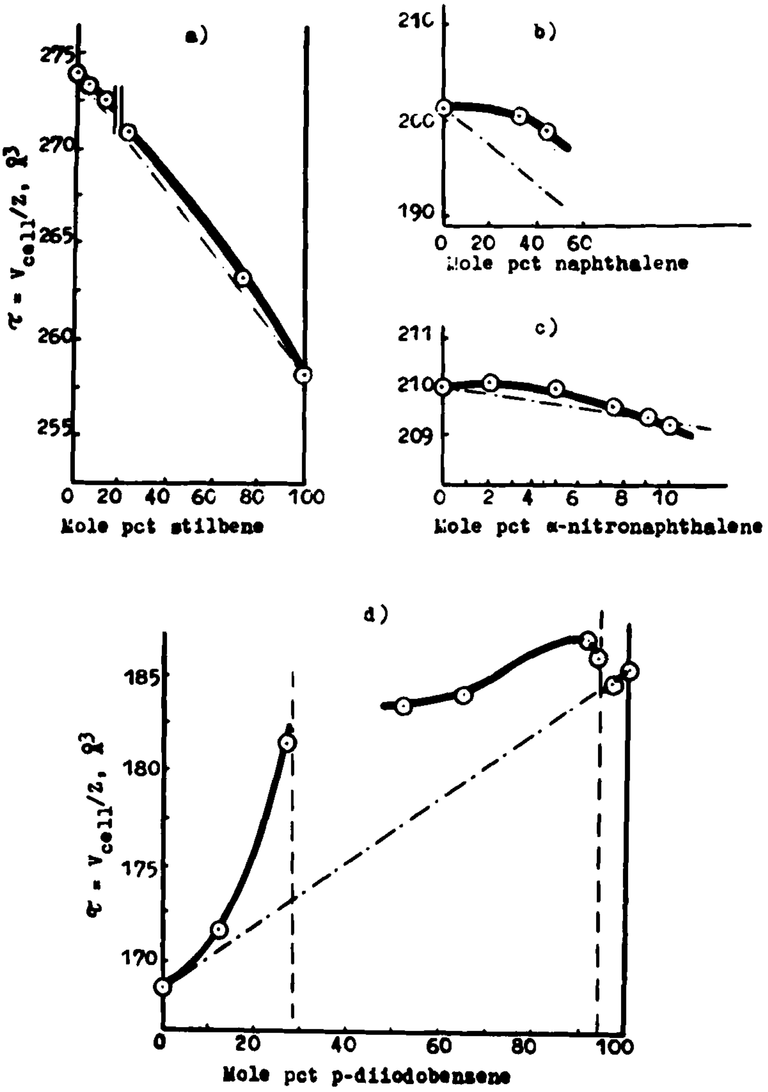

FIGURE 3 Variations of $\tau(x)$ in the systems with limited solubility: (a) dibenzyl-stilbene;[7] (b) naphthalene-2-Cl-naphthalene, the phase with the 2-Cl-naphthalene structure;[4] (c) acenaphthene-α-nitronaphthalene, the phase with the acenaphthene structure;[11] (d) *p*-dibrombenzene-*p*-diiodobenzene.[9]

plain the non-trivial *S*-shaped (relative to τ_l) curves in Figures 1a,b,d proves to be possible only from analysis of the molecular packing in the crystal.

The presence of closely packed layers in the plane *ab* of the unit cell (in the space group $P2_1/a$) is a common characteristic feature of the structure of condensed aromatic molecules. In this case long molecular axes are approximately perpendicular to the layer plane. The crystal structure of naphthalene may serve as a model for this series of substances. If at $V_G > V_M$ the shape of molecule *G* is such that its positioning in place of molecule *M* in the solid solution crystal leads to shortened intermolecular contacts in the layer *ab*, then a pronounced increase of $\tau(x)$ is observed (as compared to τ_l). As this takes place, mainly the periods *a* and *b* of a unit cell change.

For instance, in the structure of acridine-II [20] the molecular packing in the layers is such that the —H atoms of the neighboring molecules fall on both sides into the "hollow" near the $\gtrless$N atom of the acridine molecule. The anthracene guest molecules have no such hollow. Therefore, on formation of the solid solution crystal each anthracene guest molecule has to push a part its nearest neighbors, distorting the lattice in 3–5 coordination spheres. X-ray measurements show[8] that $a \cdot \sin \beta$ increases from 16.35 ± 0.01 Å to 17.08 ± 0.01 Å; *b* from 18.51 ± 0.01 Å to 19.60 ± 0.01 Å; the period *c* shows practically no changes (6.07 → 6.08 Å). Figure 2a presents the curves $\tau(x)$ for solid solutions of acridine (on the left) and anthracene phases of the acridine–anthracene system. Solid solutions with the acridine structure may contain no more than 5 mol.% of anthracene, whereas in the anthracene matrix the impurity concentration comes to 72%. The molecules of acridine and anthracene are so similar in shape and dimensions, that the "hollow" does not preclude the guest acridine molecules to adapt the anthracene structure up to large concentrations. But, as shown above, the anthracene molecules are "packed tight" in the acridine structure. The details of the geometrical analysis of substitution for this system have been published elsewhere.[8]

In the naphthalene type structures the packing of the molecular layers by translation along *c* occurs with a lesser density. For instance, in the naphthalene structure the shortest non-bonded atom–atom contacts between different layers ($C \cdots H = 3.15$ Å and $H \cdots H = 2.55$ Å) even exceed the sum of the corresponding van der Waals radii. In these contacts β-atoms of molecules are involved. Therefore, if the impurity is a β-R-napthalene with small substituent —R(—OH, —F), then at low impurity concentrations, when the β-atoms are involved only in

M–M or *G–M* type interlayer contacts there arise conditions for closer packing of the layers. The shape of the curve $\tau(x)$ for these concentrations lags behind τ_l, Figure 1a, though $V_G > V_M$. With increasing x, the probability of meeting and contacting β-R impurity molecules of neighboring layers increases. It is becoming tight in the interlayer space, which causes an *S*-shape bending of the curve $\tau(x)$, resulting in its positive deviation from τ_l. The retardation of $\tau(x)$ from τ_l at high concentrations of β-naphthol, when naphthalene molecules are regarded as an impurity, has been accounted for earlier: $V_G < V_M$. It is clear that if two isostructural substances form a continuous series of solid solutions, the separation of the molecules into *M* and *G* should be done only for illustrative interpretation of the results. Note that in solid solutions of this type the axis *c* of the unit cell should undergo the most marked change. This conclusion is confirmed by X-ray measurements.[14]

It has been found that the high-temperature forms-I of many β-derivatives of naphthalene are isostructural relative to the naphthalene itself. In this case the noncentrosymmetric molecules of β-R-naphthalene (R = OH, F, Cl, Br *et al.*) fulfill statistically the $\bar{1}$ site symmetry of the naphthalene molecule due to orientational disorder.[21–23] However, not all the pairs of these isostructural substances give a phase diagram with continuous solubility. Of great importance here are the particular details of disorder in the structure of individual compounds. It is these details which determine the possibility of fitting neighboring molecular layers to one another. Therefore, polymorphic transition I–II with decreasing temperature results merely in doubling of the period *c*, i.e., in an uniquely defined arrangement of the groups —R in the crystal.[23]

It is essential that in solid solutions formed by β-derivatives of naphthalene, the lattice period *c* undergoes very marked changes. The curves $\tau(x)$ are either *S*-shaped, Figure 1a,b, or exhibit a positive deviation from τ_l at all concentrations, Figure 1e.

The curves *c* and *d* in Figure 1 refer to systems which involve acyclic dicarboxylic acids with even number of carbon atoms: adipinic $C_6H_{10}O_4$, suberic $C_8H_{14}O_4$, sebacic $C_{10}H_{18}O_4$ and dodecanedioic $C_{12}H_{22}O_4$. The structures of these acids are isomorphous.[1,18] The molecules are hydrogen-bonded to form infinite chains extended along the axis *c*. As usual, the presence of hydrogen bonds does not preclude the fulfillment of the close packing principle: there exist even somewhat shortened atom–atom contacts between the molecules belonging to neighboring chains. In other words, it is impossible to find directions with greater or lesser packing density in the structure. Therefore, in solid solutions of these substances all the three lattice periods undergo distortion, rather than the axis *c* alone,[16] though the molecules of the substances differ only in length and the direction of their long axes coincides with the period *c*. The breakdown of side contacts on substitution of some molecules by longer (or shorter) ones causes distortion of all the lattice parameters. No linear variation of $\tau(x)$ results from such distortions, Figure 1c,d.

The least deviations of the experimental dependence $\tau(x)$ from τ_l have been found for the dibenzyl–stilbene system, Figure 3a. This is due to the flexibility of the molecules of both components, which simplifies adjusting the impurity molecules to the packing of the matrix molecules. Indeed, the X-ray structure analysis on solid solution crystals of this system show a gradual change in conformation of the "effective" molecule with composition.[24]

In the tolan (*A*)–diphenylmercury (*B*) system the molecules of the components are practically identical in dimensions. With equal width and thickness, molecule *A* is shorter than molecule *B* only by 0.2 Å; this difference does not exceed the variations normally observed for van der Waals' radii. In this case $\tau_A > \tau_B$, Figure 2b: the crystal structures of the components differ markedly. The Hg atoms in structure *B*[25,26] have no contacts with the neighboring molecules. Therefore, the somewhat larger acetylene group —C≡C— of the guest molecule *A*, when substituting —Hg— in structure *B*, produces no distortions. But in the process of substitution there appear vacancies in the packing of the molecular ends (*A* is shorter than *B*) which result in deviation of the curve $\tau(x)$ in the direction opposite to the inclination of τ_l, the right-hand side in Figure 2b.

Finally, one should pay attention to the cases where, it is impossible, proceeding only from the molecular packing, to account for the shape of the curve $\tau(x)$ e.g., to explain the origin of the maxima observed: Figure 1b, Figure 1c; the left-hand side of Figure 2b, the middle phase in Figure 3d. It has been found experimentally[9,27] that the maxima on the curves $\tau(x)$ for the tolan phase, Figure 2b, and for the intermediate γ-phase, Figure 3d, correspond to the minima on the variation of the temperature factor $B(x)$ with concentration. Such anomalies are associated with noticeable changes in the lattice vibrations. Besides, a possible reason may be the appearance of the short-range order regions observed, for instance, in solid solutions of the tolan phase.[28]

Unfortunately, there still appear noncrystallographic papers, whose authors apply *a priori* the additive law of lattice distortions in organic solid solutions to a wide range of concentrations. The results of the analysis presented show that such an approach is erroneous. The following should be pointed out. An analysis of optimal ways of substitution, with due allowance for peculiarities of the matrix structure, makes it possible in many cases to account for the shape of the curve $\tau(x)$ obtained experimentally. But the predictive power of such an analysis cannot yet give an unambiguous answer even with a series of compounds similar in the molecular packing. The probability of correct predictions may improve after accumulating and generalizing more extensive experimental material. However, as with solid solutions of inorganic substances, it is hardly likely that a unique model can be developed which will enable one to calculate the exact shape of the curve $\tau(x)$ for any binary organic system.

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