Molecular Crystals and Liquid Crystals

Binary Phase Diagrams of Some Molecular Compounds—II

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Binary Phase Diagrams of Some Molecular Compounds—II

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Abstract—The (i) anthracene–*d*-camphor, (ii) naphthalene–*β*-naphthol, (iii) anthracene–hexachlorobenzene and (iv) *d*-camphor–hexachlorobenzene phase diagrams have been determined by calorimetric measurements, optical microscopy and X-ray diffraction. The effect of the crystal symmetry, molecular volume and molecular shape of the component species on the extent of the terminal solid solutions is considered. In all systems the packing factor between the components is high (>0.92), but only in the case of naphthalene and *β*-naphthol are the molecules of similar shape. In this system a peritectic horizontal occurs at 367.3 K and extends from 42.5 to 72.5 mole pct *β*-naphthol, the limits of solubility at 298 K being 57.0 mole pct *β*-naphthol in naphthalene and 16.5 pct naphthalene in *β*-naphthol. The other three pairs of compounds form simple eutectics. In the anthracene–*d*-camphor system a eutectic point occurs at 81.5 mole pct camphor and 400.0 K and the limits of solid solubility at this temperature are 3 mole pct camphor in anthracene with practically no solubility in the reverse case. Anthracene and hexachlorobenzene form a eutectic at 51.0 mole pct anthracene and 441.5 K and the limits of solid solubility are 0.5 mole pct of each component in the other at the eutectic temperature. Hexachlorobenzene and *d*-camphor form a eutectic at 78.5 mole pct *d*-camphor and 409.0 K, the limits of solid solubility being 9 mole pct *d*-camphor in hexachlorobenzene and 0.5 mole pct hexachlorobenzene in *d*-camphor.

1. Introduction

The general conclusions drawn from the phase diagrams described in Part I[1] were that volume relationships are decisive in determining solid solubilities between molecular compounds and that when molecular volumes are comparable, extensive, though not complete,

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solid solubility can occur even if symmetry requirements are not fulfilled. This is in agreement with the predictions of Kitaigorodskii.[2] We considered previously[1] three binary systems in which the packing factors between the molecules, defined as $1 - \Delta/\tau$, where Δ is the difference in molecular volumes and τ is the volume of the larger molecule, were 0.61, 0.69 and 0.94. Only when the packing factor was high did extensive solid solubility occur, although in this case (anthracene–carbazole) the symmetry requirements for complete solid solubility were not met.

The extent of solid solubility is influenced by the shapes of the two species of molecules in the solid solution as well as the relative molecular volumes. The four binary systems discussed in the present paper were chosen because the packing factors are all high (> 0.92) but the relative shapes of the molecules vary from system to system, the molecules being similar in both size and shape only in the case of naphthalene and β-naphthol.

The extent of solid solubility in the systems (i) anthracene–d-camphor, (ii) naphthalene–β-naphthol, (iii) anthracene–hexachlorobenzene and (iv) d-camphor–hexachlorobenzene was measured by determining the binary phase diagrams. The procedures for preparing the alloys and the calorimetric techniques used to determine the solidus and liquidus followed closely those described in Part I.[1] In addition, X-ray diffraction and optical microscopy were used, where applicable, to determine the phase boundaries in the solid.

2. Anthracene and d-Camphor

Anthracene and d-camphor have different molecular and crystal symmetries. The anthracene molecule consists of three conjugated six-membered rings and the crystal symmetry is monoclinic ($P2_1/a$), while camphor has an almost spherical molecule and a cubic crystal symmetry ($F\bar{4}3m$). The volume occupied by each anthracene molecule, calculated from the size of the unit cell ($a = 8.561$ Å, $b = 6.036$ Å, $c = 11{,}163$ Å, $\beta = 124°\ 42'$)[3] is 236 Å^3 compared with that for camphor ($a = 10.0$ Å) of 250 Å$^{3[4]}$, the packing factor is, therefore, close to unity (Table 1).

The phase diagram, determined from calorimetric measurements as previously described,[1] is shown in Fig. 1. A eutectic occurred

TABLE 1   The Crystal Symmetries, Packing Factors and Limits of Solid Solubility in some Binary Systems between Molecular Compounds.

System	Crystal structure	Mol. per unit cell	Packing factor	Solid solubility (mole pct)
Anthracene	Monoclinic ($P2_1/a$)	2	0.94	22.0
Carbazole	Orthorhombic (Pnam)	4		24.0
Anthracene	Monoclinic ($P2_1/a$)	2	0.69	2.9
Naphthalene	Monoclinic ($P2_1/a$)	2		0
Anthracene	Monoclinic ($P2_1/a$)	2	0.94	3.0
Camphor	F.C.C. (F$\bar{4}$3m)	4		0
Anthracene	Monoclinic ($P2_1/a$)	2	0.97	0.5
Hexachlorobenzene	Monoclinic ($P2_1/c$)	2		0.5
Naphthalene	Monoclinic ($P2_1/a$)	2	0.95	57.0
β-Naphthol	Monoclinic ($P2_1/a$)	8		16.5
Naphthalene	Monoclinic ($P2_1/a$)	2	0.61	12.0
Camphor	F.C.C. (F$\bar{4}$3m)	4		6.0
Hexachlorobenzene	Monoclinic ($P2_1/c$)	2		9.0
Camphor	F.C.C. (F$\bar{4}$3m)	2	0.92	0.5

at 81.5 mole pct camphor and 400 K and the limits of solid solubility at this temperature were 3 mole pct camphor in anthracene with practically no solid solubility in the reverse case.   Examination of the microstructures of the alloys indicated that the solid solubilities at room temperature were approximately the same, see for example Fig. 2.   At least six determinations of the solidus and liquidus temperature were carried out for each alloy.   Although the overall reproducibility of results varied slightly from alloy to alloy because of segregation, the standard deviation of the mean of determinations for any one ingot was generally less than 0.7 K for the solidus and 0.8 K for the liquidus.

The eutectic composition and limits of solid solubility in binary systems are sometimes difficult to establish precisely from measurements of the solidus and liquidus but additional evidence may be found by determining the relative amounts of eutectic in the various alloys.[1]   The enthalpy of fusion of the eutectic portion of the alloys,

which is directly proportional to the amount of eutectic present, is plotted against composition in Fig. 3, the reproducibility of the enthalpy of fusion measurements being ± 3 pct. Extrapolation of the line of least squares through the experimental points indicates that no eutectic would be detectable in the 3 mole pct camphor alloy, in agreement with the results presented in Fig. 1. The maximum enthalpy of fusion of 9.35 kJ mole^{-1} occurred at 81.5 mole pct camphor, which is, therefore, the eutectic composition.
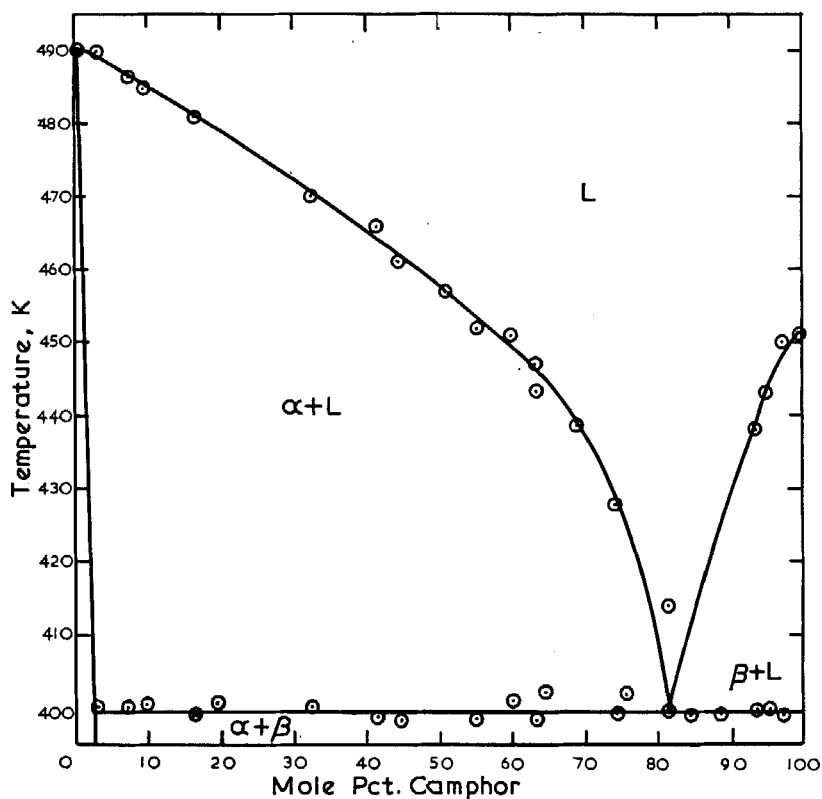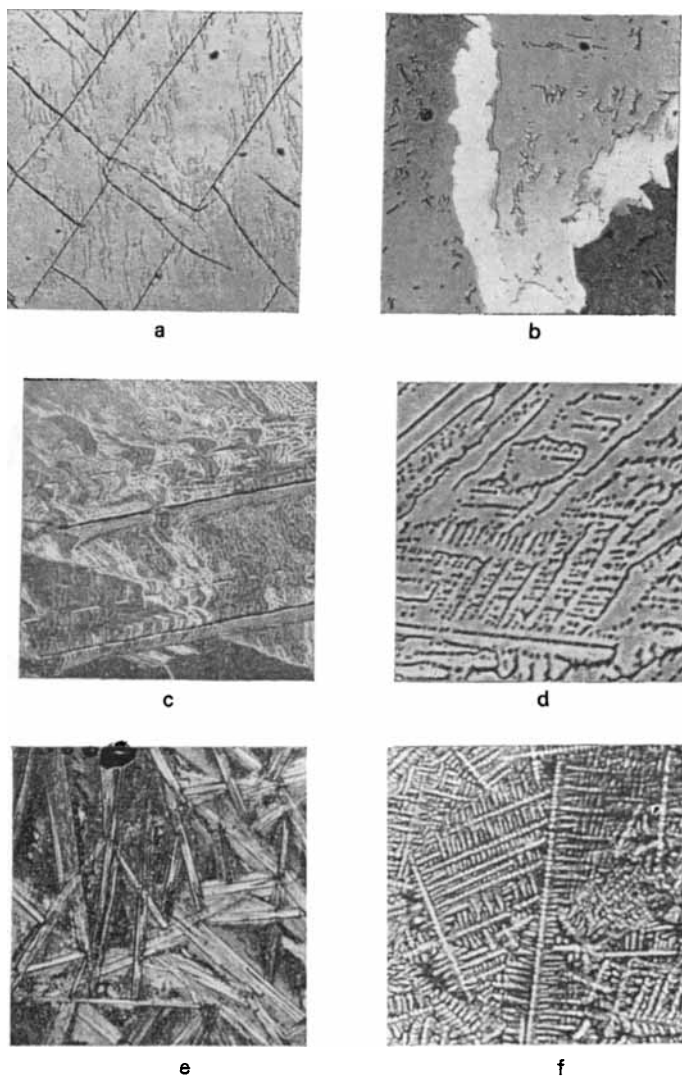

Figure 1. The anthracene-d-camphor phase diagram.

Figure 2. Microstructures of (a) naphthalene—90 mole pct β-naphthol alloy, single phase ×80; (b) naphthalene—65 mole pct β-naphthol alloy, β phase with α formed around grain boundaries ×80; (c) anthracene—74.5 mol: pct d-camphor alloy, plates of pro-eutectic anthracene rich α phase plus eutectic ×80; hexachlorobenzene—78.5 mole pct d-camphor alloy, eutectic mixture of α (dark) and β (light) ×200; (e) hexachlorobenzene—35.6 mole pct d-camphor alloy, plates of pro-eutectic hexachlorobenzene rich α phase plus eutectic ×80; (f) hexachlorobenzene—90.0 mole pct d-camphor alloy, plates of pro-eutectic dendrites of camphor rich β phase plus eutectic ×80.
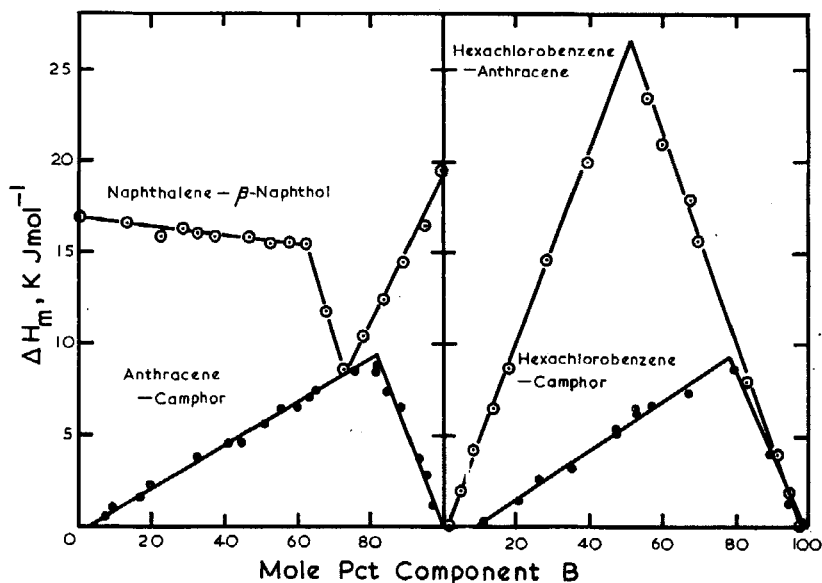
Figure 3. The enthalpy of fusion of the eutectic portion of the alloys in the anthracene–d-camphor, hexachlorobenzene–anthracene and hexachloro-benzene–d-camphor systems and the enthalpy of fusion of the whole alloy in the naphthalene–β-naphthol system as a function of composition.

3. Naphthalene and β-Naphthol

Naphthalene, which consists of two conjugated six-membered rings, and its hydroxy derivative β-naphthol both have monoclinic crystal structures ($P2_1/a$), however, naphthalene has 2 molecules per unit cell and β-naphthol has 8.[5,6] The volume occupied by the naphthalene molecule, calculated from the size of the unit cell ($a = 8.235$ Å, $b = 6.003$ Å, $c = 8.658$ Å, $\beta = 122°\ 55'$),[5] is 180 Å³ compared with 191 Å³ for β-naphthol ($a = 8.185$ Å, $b = 5.950$ Å, $c = 36.29$ Å, $\beta = 119°\ 52'$[6]), giving a packing factor of 0.95 (Table 1).

The solidus and liquidus in the binary system and the enthalpies of fusion of the alloys were determined from calorimetric heating curves, with at least four determinations being carried out for each alloy. The standard deviation of the mean of measurements for any one alloy was less than 0.2 K for the solidus, 0.5 K for the liquidus

and 0.46 kJ mole^{-1} for the enthalpies of fusion. The enthalpy of fusion of β-naphthol, which has not been reported previously, was 19.35 ± 0.5 kJ mole^{-1}.

The phase boundaries in the solid at 298 K were determined by optical microscopy (Fig. 2) and by X-ray diffraction. The crystal lattice parameters of the terminal solid solutions were determined from X-ray powder diffraction photographs taken in a Guinier-Hägg focussing camera, using thoria as an internal standard. Only the positions of those lines which were moderately intense and which could be indexed unambiguously were measured, about fifteen in each photograph. From these line positions the " best " lattice parameters were computed by a simple least squares procedure. The absolute accuracy of these determinations, judged by comparison with the accepted values for the pure materials, is not high ($\sim 0.3\%$) but internal consistency is much better ($\sim 0.05\%$) so that the variations in lattice parameter with composition should be substantially correct.

The variation of the lattice parameters with composition is shown in Fig. 4. It may be noted that some of these parameters appear to alter even over composition ranges (e.g. 57–62.5 pct) where both phases were undoubtedly present: this suggests that some segregation has occurred so that the actual composition of the phases differs slightly from the nominal composition.

The phase diagram resulting from combined calorimetric, X-ray diffraction and optical microscopy measurements is shown in Fig. 5. Naphthalene and β-naphthol form a peritectic rather than the complete range of solid solutions reported previously.[7,8] This confirms Kitaigorodski's prediction[9] that in this system complete solid solubility cannot occur because the requirement that the two components have the same number of molecules in the unit cell is not met. The peritectic horizontal occurred at 367.3 K and extended from 42.5 to 72.5 mole pct β-naphthol. The limit of solid solubility of β-naphthol in naphthalene at 298 K was 57 mole pct and that of naphthalene in β-naphthol was 16.5 mole pct.

The plot of enthalpy of fusion against composition showed discontinuities corresponding to the phase boundaries in the solid just below the melting point (Fig. 3), but the discontiniuty associated with the low β-naphthol end of the peritectic horizontal was difficult
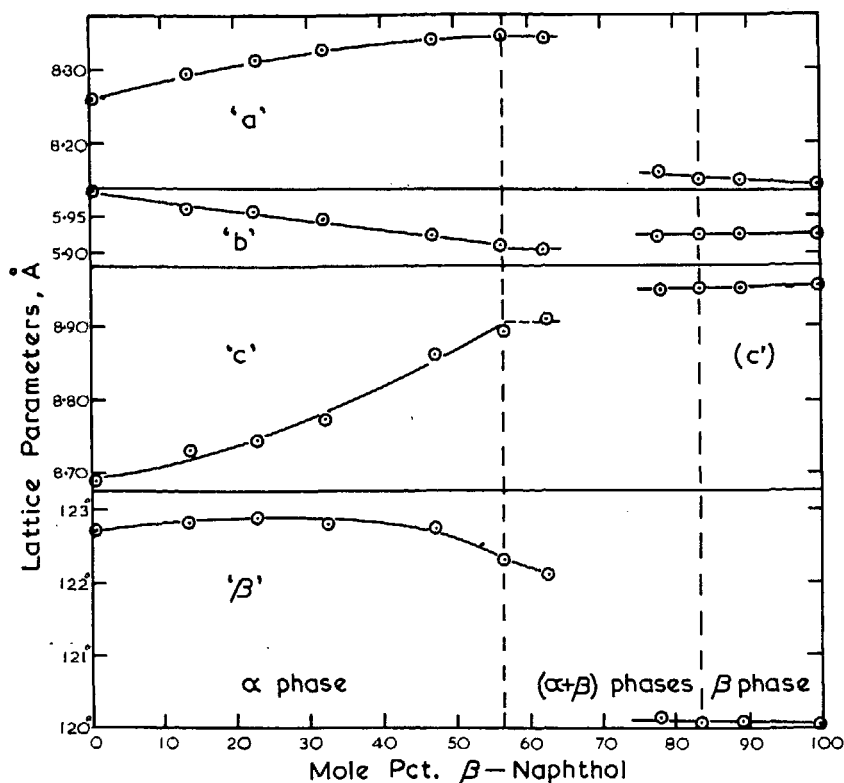
Figure 4. Variation of crystal lattice parameters with composition in the naphthalene–β-naphthol system. (Note that for β-naphthol rich terminal solid solution $c' = \frac{1}{4}c$ is used as ordinate.) Broken lines indicate limits of solid solubility at room temperature.

to detect. The heat effect associated with the peritectic decomposition of β into α solid solution was calculated to be 9.70 ± 0.42 kJ mole^{-1}, using the phase diagram in Fig. 5 and the experimentally determined enthalpies of fusion.

4. Hexachlorobenzene and Anthracene

Hexachlorobenzene has a monoclinic crystal structure $(P2_1/c)$[10] and the volume occupied by each molecule calculated from the size of the unit cell ($a = 8.07$ Å, $b = 3.84$ Å, $c = 16.61$ Å, $\beta = 116°\ 52'$)[10] is 230 Å^3. The packing factor in alloys between anthracene and
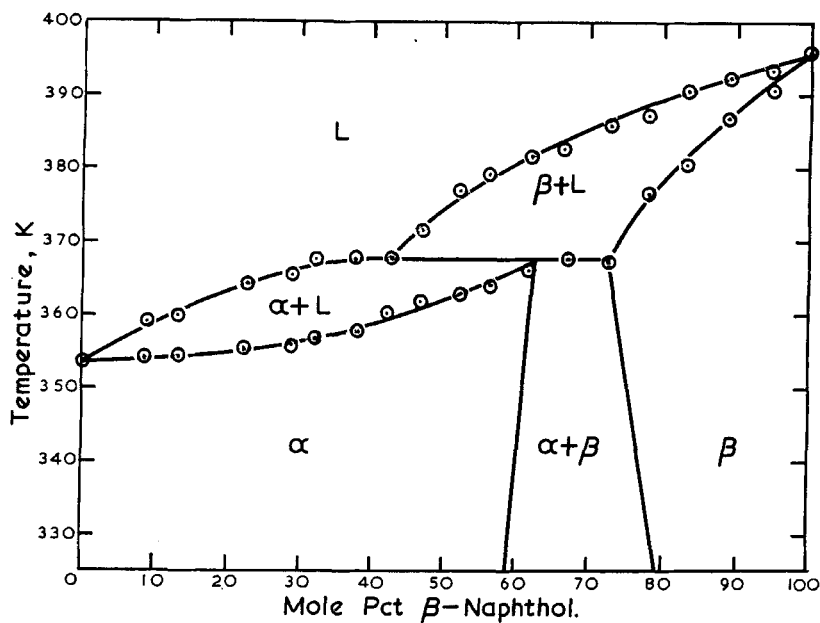
Figure 5. The naphthalene–β-naphthol phase diagram. Phase boundaries in the solid determined by optical microscopy and X-ray diffraction.

hexachlorobenzene is, therefore, high (0.97), although the molecules are not similar in shape (Table 1, Fig. 6).

The solidus and liquidus in the hexachlorobenzene-anthracene diagram were determined from calorimetric heating curves and the position of the eutectic point and the limits of solid solubility were confirmed by plotting the enthalpy of fusion of the eutectic portion of the alloys against composition (Figs. 7 and 3). The eutectic occurred at 51.0 mole pct anthracene and 441.5 K and the limits of solid solubility at the eutectic temperature were 0.5 mole pct of each component in the other. The standard deviation from the arithmetic mean of determinations for any one alloy was 0.5 K for the solidus and 1.0 K for the liquidus and the reproducibility of the enthalpy of fusion measurements was ± 3 pct.

5. Hexachlorobenzene and *d*-Camphor

The packing factor for alloys between these two compounds is 0.92. (Table 1). Measurements similar to those described above were
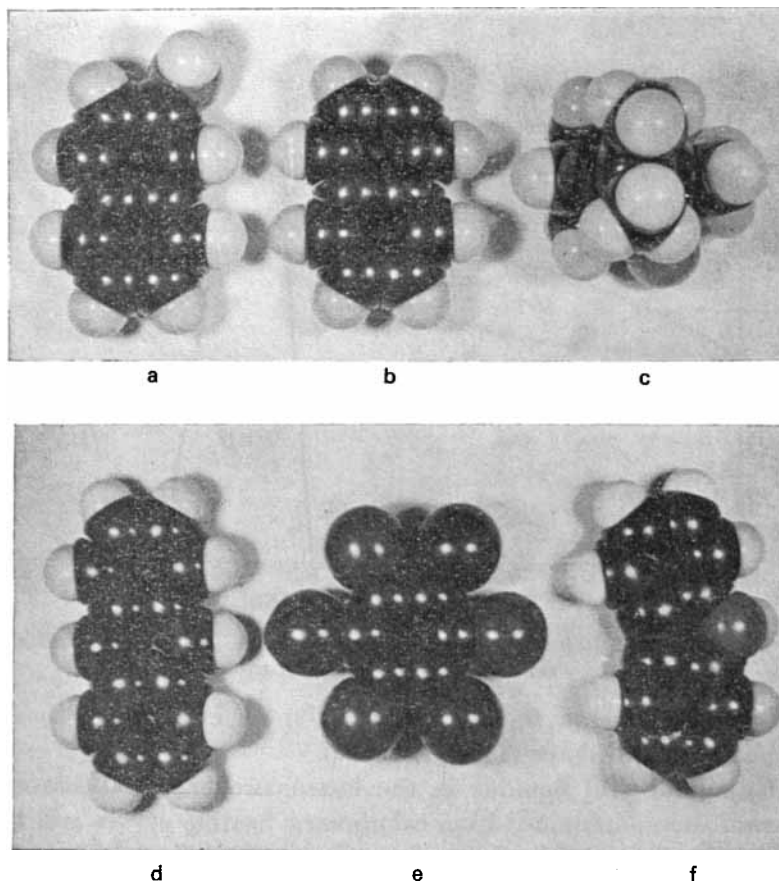
Figure 6. Models of molecules of (a) β-naphthol, (b) naphthalene, (c) d-camphor, (d) anthracene, (e) hexachlorobenzene, and (f) carbazole.

made on alloys in this system, and the results are shown in Figs. 8 and 3. A eutectic point occurred at 78.5 mole pct d-camphor and 409 K and the limits of terminal solid solubility at this temperature were 9 mole pct d-camphor in hexachlorobenzene and 0.5 mole pct hexachlorobenzene in d-camphor. Examination of the microstructures of the alloys, which were similar to those found in the anthracene–camphor and naphthalene–camphor systems (Fig. 2), indicated that the solid solubilities were similar at room temperature.

As in the d-camphor–anthracene system, a tendency towards segregation gave rise to fluctuations in the measured values for
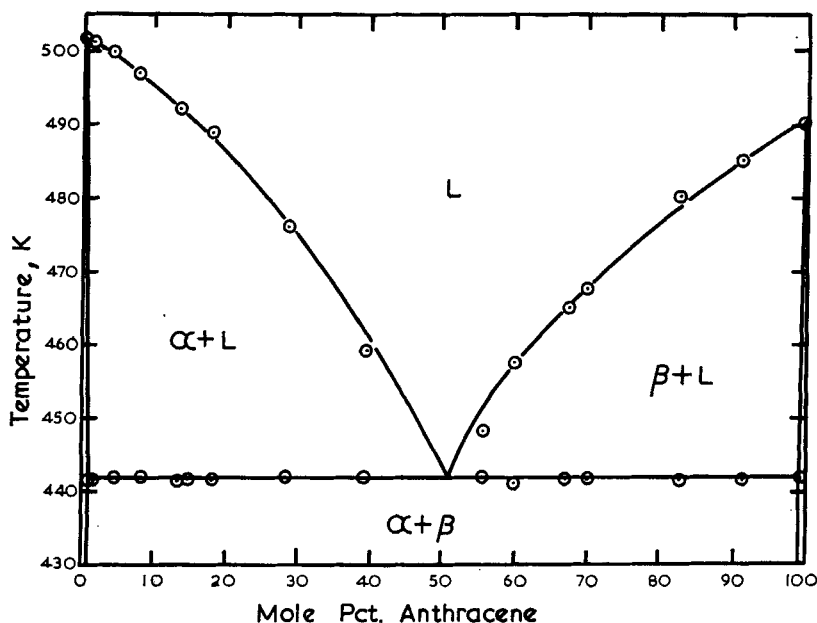
Figure 7. The hexachlorobenzene–anthracene phase diagram.

samples from any one ingot.   The values shown in Figs. 8 and 3 represent the mean of at least six independent measurements, the standard deviation being 1.0 K for the solidus temperature and 2.0 K for the liquidus temperature and the reproducibility of the enthalpy of fusion measurements being ± 4 pct.

5. Discussion

The crystal symmetries, packing factors and limits of solid solubility for the seven binary systems dealt with in this and the previous paper[1] are listed in Table 1 and the molecular shapes are shown in Fig. 6.   The symmetry requirements for complete solid solubility, as discussed by Kitaigorodskii[2,9] and in Part I[1] are fulfilled only in the case of the anthracene–naphthalene system.   In this system, however, the molecular volumes of the two components are different and the solid solubilities are low.[1]   This, taken in conjunction with the results for the anthracene–carbazole and naphthalene–camphor systems (Table 1), led to the conclusion in Part I that, in the absence
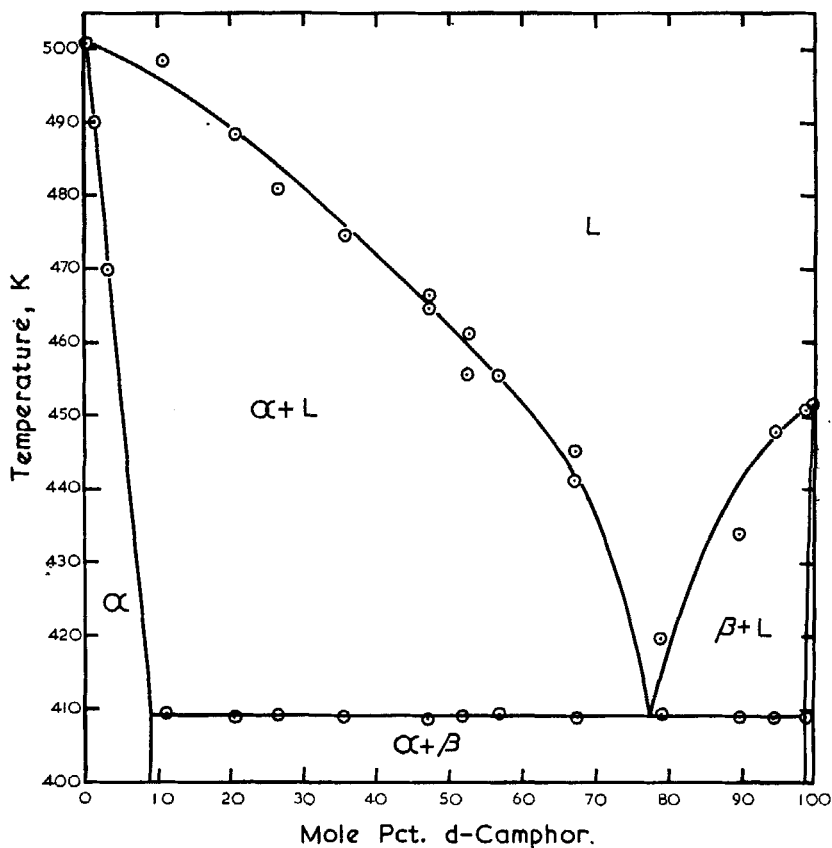
Figure 8. The hexachlorobenzene–*d*-camphor phase diagram.

of complete solid solubility, the extent of the terminal solid solution
is governed by the relative molecular volumes of the two com-
ponents rather than by symmetry considerations.

In each of the four systems under consideration in the present
paper, the molecular volumes of the components are similar, leading
to high packing factors, although the molecular shapes are com-
parable only in the case of naphthalene and β-naphthol (Table 1,
Fig. 6). The occurrence of extensive solid solubility in the latter
case alone suggests that it is necessary for the two components to be
similar in molecular shape as well as molecular volume before they
are mutually soluble to any extent.

The results for the anthracene–camphor and naphthalene–camphor systems (Table 1) suggest that in some cases a degree of compatibility in molecular shape may be more important than a similarity in overall molecular volume in determining the extent of solid solubility. The crystal and molecular symmetries of the components are identical in these two systems but the packing factor is 0.94 for the former and only 0.61 for the latter. However, in the naphthalene–camphor system there is some compatibility between the shapes of the two molecules, the longest dimension of the naphthalene molecule being almost the same as that of the camphor molecule, and the terminal solid solubilities are larger than in the anthracene–camphor system where there is no compatibility between the molecular shapes.

Kitaigorodskii[2,9] has predicted that complete solid solubility between molecular compounds will occur only if the crystals have the same space group and number of molecules per unit cell and if the molecules of the two compounds are similar in size and shape. An apparent exception to this may occur if the molecules of one, and only one, of the components are enantiomorphic. The present results indicate that if the symmetry requirements for complete solid solubility are not fulfilled, extensive terminal solid solubility will occur only if the molecular volumes of the components are similar and if the molecular shapes are compatible.

REFERENCES

1. Robinson, P. M., Rossell, H. J. and Scott, H. G., *Mol. Cryst. and Liq. Cryst.* **10**, 61 (1970).
2. Kitaigorodskii, A. I., *Organic Chemical Crystallography*, English translation by Consultants Bureau Inc., New York (1961).
3. Sinclair, V. C., Robertson, J. M. and Mathieson, A. McL., *Acta Cryst.* **3**, 251 (1950).
4. Dunning, W. J., *Phys. Chem. Solids* **18**, 21 (1961).
5. Abrahams, S. C., Robertson, J. M. and White, J. G., *Acta Cryst.* **2**, 238 (1949).
6. Watson, H. C. and Hargreaves, A., *Acta Cryst.* **11**, 556 (1958).
7. Rudolfi, E., *Z.S. Physik. Chem.* **66**, 705 (1909).
8. Rheinbolt, H. and Kircheisen, M. J., *Prakt. Chem.* **113**, 348 (1932).
9. Kitaigorodskii, A. I., *Dokl. Akad. Nauk SSSR* **113**, 604 (1957).
10. Tulinsky, A. and White, J. G., *Acta Cryst.* **11**, 7 (1958).