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Isomorphism in the High-temperature Forms of Molecular Complexes between Aromatic Hydrocarbons and Various Electron Acceptors Arising from Molecular Motion

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In addition to the six crystalline pyrene complexes reported earlier, the high-temperature forms of the following nineteen 1:1 molecular complexes have been found to be isomorphous to each other; the pyrene complexes with 1,3,5-trinitrobenzene, 2,4,6-trinitrophenol, 4-nitrophthalic anhydride, pyromellitic dianhydride, 5-nitrobenzofuroxan, 4,6-dinitrobenzofuroxan, and benzotrifuroxan, the fluoranthene complexes with 2,4-dinitrophenol, 1,3,5-trinitrobenzene, 2,4,6-trinitrochlorobenzene, 2,4,6-trinitrophenol, 2,4,6-trinitrotoluene, 4-nitrophthalic anhydride, pyromellitic dianhydride, 4,6-dinitrobenzofuroxan, and benzotrifuroxan, and the phenanthrene complexes with 1,3,5-trinitrobenzene, 2,4,6-trinitrophenol, and 4,6-dinitrobenzofuroxan. Furthermore, metastable isomorphous forms were obtained in the process of the solidification of the melt of the following three complexes: fluoranthene-5-nitrobenzofuroxan, phenanthrene-2,4,6-trinitrotoluene, and phenanthrene-4-nitrophthalic anhydride. Rather large entropies of the transitions to these unique high-temperature forms, up to 57 J mol^{-1} K^{-1}, are often comparable with the entropies of melting, 46—67 J mol^{-1} K^{-1}. The isomorphism in these twenty-eight complexes is demonstrated by essentially identical and very simple X-ray diffraction patterns and/or by the formation of continuous solid solutions between pairs of these forms. A trigonal lattice is proposed as the probable structure of these high-temperature forms. A broad-line ^{1}H NMR study clearly showed that the unusual features of these isomorphous forms are mostly associated with the onset of a large degree of molecular motion at the transition temperatures.

We reported earlier that the crystalline pyrene complexes with 2,4-dinitrofluorobenzene, 2,4-dinitrochlorobenzene, 2,4-dinitrophenol, 2,4-dinitrotoluene, and 2,4,6-trinitrochlorobenzene exhibit polymorphic transitions and become isomorphous to each other above the transition temperatures.[1] Isomorphism in molecular complexes is not unknown; however, the cases so far reported are limited to the complexes of closely related component compounds. For example, the 1,3,5-trinitrobenzene and 2,4,6-trinitrophenol complexes of naphthalene, pyrene, and fluoranthene have each been shown to be isomorphous by Herbstein and Kaftory.[2] This relationship has been established for the crystals stable at room temperature. The phenomenon found by us is apparently different from this kind of isomorphism. Except for the 2,4-dinitrochlorobenzene complex, the transitions are associated with rather large enthalpy and entropy changes: 12—18 kJ mol^{-1} and 37—50 J mol^{-1} K^{-1}, which are of the same order of magnitude as the corresponding values of melting: 18—25 kJ mol^{-1} and 50—59 J mol^{-1} K^{-1} respectively. On the basis of these thermodynamic data, we speculated that the specific interaction between the hydrocarbon molecule and the substituent on the acceptor molecule disappears because of the dynamical averaging of the interaction by a large degree of thermal motion in the high-temperature forms. Later, the onset of such a molecular motion was firmly established by the drastic decreases in the second moments in broad-line ^{1}H NMR spectra at the transition temperatures.[3] Moreover, the 2,4,6-trinitrotoluene complex was added to the list of this interesting class of molecular complexes. Continuing the search for such complexes, nineteen more complexes have been found to behave similarly. All the complexes studied before are composed of pyrene and one of the derivatives of *m*-dinitrobenzene or 1,3,5-trinitrobenzene; however, we have now succeeded in finding complexes containing hydrocarbons other than pyrene, such as phenanthrene-2,4,6-trinitrophenol and fluoranthene-1,3,5-trinitrobenzene, and also complexes containing an acceptor bearing no nitro group, such as pyrene-pyromellitic dianhydride and fluoranthene-benzotrifuroxan. Thus, the appearance of this kind of isomorphism needs neither a common-component compound nor a close similarity between components. The present paper gives an account of an examination of the thermodynamic data of the transition and melting, the X-ray diffraction pattern, the solid-solution formation, and the broad-line ^{1}H NMR study of the newly found complexes.

Experimental

Materials. The donors employed were pyrene (Py), fluoranthene (Fl), and phenanthrene (Ph), while the acceptors were 2,4-dinitrophenol (DNP), 1,3,5-trinitrobenzene (TNB), 2,4,6-trinitrochlorobenzene (TNC), 2,4,6-trinitrophenol (TNP), 2,4,6-trinitrotoluene (TNT), 4-nitrophthalic anhydride (NPA), pyromellitic dianhydride (PMDA), 5-nitrobenzofuroxan (NBF), 4,6-dinitrobenzofuroxan (DNBF), and benzotrifuroxan (BTF). Their structural formulas are presented in Fig. 1. The Py, Eastman white label, was recrystallized from xylene. The Ph, Eastman white label, was boiled with maleic anhydride in xylene to remove any anthracene.[4] TNB was prepared, starting from TNT, through 2,4,6-trinitrobenzoic acid.[5] The TNT, Eastman yellow label, was purified by recrystallization from ethanol. The NPA and PMDA were sublimed in a vacuum just before use. The NBF, DNBF, and BTF were prepared following the procedures reported by Bailey and Case.[6] The other reagents obtained from commercial sources were employed without further purification. The complexes were crystallized by mixing the component compounds dissolved in appropriate solvents or by melting mixtures of equimolar amounts of the component compounds.

Measurements. Calorimetric, X-ray, and NMR measurements were carried out as described in our previous papers.[1,3] Density measurements of four complexes with transition temperatures lower than 60 °C were made using Gay-Lussac pycnometers. A small amount of a detergent had to be added to the water employed as the immersion fluid in order to wet the crystals. Air bubbles trapped by the crystals were eliminated by repeated evacuations and then by leaving the pycnometers overnight under reduced pressure.

Results and Discussion

Thermodynamic Data. The complexes which become isomorphous upon transitions, including the six Py complexes found previously, are summarized in Fig. 1. Solid circles indicate that enantiotropic transitions are observable. On the other hand, broken circles show that the high-temperature forms of these complexes are metastable, as will be described later.

The transition temperatures, melting points, and associated enthalpies and entropies are collected in Table 1. Not only the six Py complexes reported previously by us, but also some other complexes are known to exhibit polymorphic transitions. Casellato *et al.* have located the transitions in the Py–TNB complex at 129 and 215.5 °C with enthalpies of 2.4 and 1.9 kJ mol^{-1} respectively, and the melting point, at 253.3 °C with an enthalpy of 38.5 kJ mol^{-1}.[7] Except for the first transition temperature, our results are in fair agreement with theirs. The transitions in the Py–TNP complex have been reported to occur at 170 and 183.4 °C, with enthalpies of 2.9 and 1.2 kJ mol^{-1} respectively, by Farrell *et al.*[8] The melting point reported by them is 233.4 °C, and the enthalpy is 32.6 kJ mol^{-1}. All our temperatures for this complex are located lower than theirs by about 5 °C. Casellato *et al.* have observed three modifications of the Py–NPA complex.[9] According to them, the I modification crystallized from a solution is transformed into the III modification at 122 °C with an enthalpy of 18 kJ mol^{-1}. The transformation into the III modification from the II obtained by cooling from the melt occurs at 105 °C. The enthalpy of the latter transition was reported to be 11 kJ mol^{-1}. Our enthalpy of the transition at 112.5 °C is a little larger than the former one reported by Casellato *et al.*, but our transition temperature is appreciably lower than theirs. We occasionally observed an additional endothermic peak at 108 °C with samples crystallized from some solvents. This peak could be detected only in the first run of the calorimetric measurements. The Py–NPA complex has been reported to melt at 179.5 °C, with an enthalpy of 24 kJ mol^{-1}, in agreement with our observation. The thermodynamic data for the Py–PMDA complex have been presented by Pelizza *et al.*; the enthalpy for the transition at 174.3 °C is 29 kJ mol^{-1}, while that of the melting at 290.4 °C is 72 kJ mol^{-1}.[10] Our enthalpy values are barely over 40 percent of theirs.

D \ A	DNF	DNC	DNP	DNT	TNB	TNC	TNP	TNT	NPA	PMDA	NBF	DNBF	BTF
Py	○	○	○	○	○	○	○	○	○	○	○	○	○
Fl			○		○	○	○	○	○	○	◌	○	○
Ph					○		○	◌	◌			○	

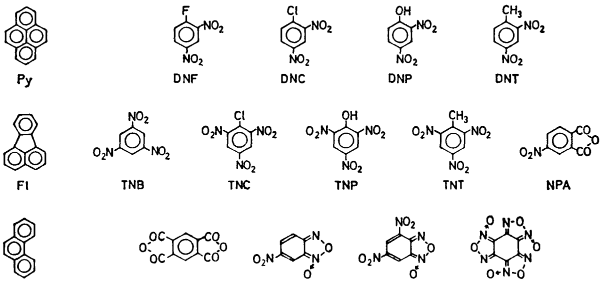

Fig. 1. The molecular complexes which become isomorphous by polymorphic transitions and the structural formulas of the component compounds.

The Fl–TNP complex has been studied by Farrell *et al.*[8] The reported transition temperature, 92.4 °C, and the enthalpy, 13.8 kJ mol^{-1}, agree well with our values. The melting point has been found at 189.2 °C, and the enthalpy, at 24.7 kJ mol^{-1}. The latter is a little larger than the present value.

The Ph–TNB complex has been reported by Kofler to exhibit a transition at 149 °C.[11] Casellato *et al.* have located it at 148.2 °C, with an enthalpy of 12 kJ mol^{-1}, while they located the melting point at 164.6 °C, with an enthalpy of 27 kJ mol^{-1}.[7] Our results in Table 1 generally agree with their values. The transition in the Ph–TNP complex has been noted also by Kofler at 106 °C.[11] The enthalpy has been estimated to be 13 kJ mol^{-1} by one of the present authors, together with an additional transition at 77 °C associated with an enthalpy of 4.6 kJ mol^{-1}.[12,13] Our new determinations well reproduced the previous results. According to Casellato *et al.*, the Ph–NPA complex melts at 96 °C, with an enthalpy of 29 kJ mol^{-1}.[9] Our results are in good agreement with theirs.

With the exception of several complexes, the entropy of transition into the unique high-temperature form is fairly large, up to 57 J mol^{-1} K^{-1}. These values are often comparable with the entropies of melting of these complexes, 46—67 J mol^{-1} K^{-1}. As the sum of all entropies of transition and melting may be supposed to be correlated with the molecular structure, it may agree with the entropy of melting of a complex which is structurally related to the present one but which does not exhibit polymorphic transitions. For example, we observed 102 J mol^{-1} K^{-1} for the Fl–DNT complex, 100 J mol^{-1} K^{-1} for the Fl-3-nitrophthalic anhydride complex, and 101 J mol^{-1} K^{-1} for the 1,10-phenanthroline–TNB complex. These values are reassuringly similar to the sum of the entropies of transition and melting of the present complexes: *e.g.*, 104 J mol^{-1} K^{-1} of the Py–DNF complex. If the latter value is appreciably smaller than the former, the occurrence of low-temperature transitions may be predictable for such a complex.

The ordinary samples of the Fl–NBF, Ph–TNT, and Ph–NPA complexes exhibit no polymorphic transition; however, the metastable high-temperature form appears when the melt is solidified. As the monotropic transition from the supercooled metastable form to the stable one is well separated from the solidification, the enthalpy and entropy associated with the melting of the metastable form could be measured. In Table

Table 1. Thermodynamic data of molecular complexes
(The values in parentheses are for monotropic transitions.)

Acceptor	Transition			Melting		
	t / °C	ΔH[c)] / kJ mol^{-1}	ΔS[c)] / J mol^{-1} K^{-1}	t / °C	ΔH[c)] / kJ mol^{-1}	ΔS[c)] / J mol^{-1} K^{-1}
			Donor: Pyrene			
2,4-Dinitrofluorobenzene[a)]	76.5	18	50	119	21	54
2,4-Dinitrochlorobenzene[a)]	41	2.4	7.5	87	18	50
2,4-Dinitrophenol[a)]	53	13	40	144	25	59
2,4-Dinitrotoluene[a)]	53.5	12	37	92.5	20	54
1,3,5-Trinitrobenzene	138 216	1.9 1.5	4.6 3.1	248	35	67
2,4,6-Trinitrochlorobenzene[a)]	79	13	40	154.5	22	50
2,4,6-Trinitrophenol	164.5 178	3.3 1.2	7.5 2.7	227	31	62
2,4,6-Trinitrotoluene[b)]	59	12	36	162	22	51
4-Nitrophthalic anhydride	112.5	20	51	177.5	24	54
Pyromellitic dianhydride	170	13	28	290	31	54
5-Nitrobenzofuroxan	89	17	47	147	23	55
4,6-Dinitrobenzofuroxan	130 185	1.7 1.0	4.2 2.1		decomp	
Benzotrifuroxan	112	5.4	14		decomp	
			Donor: Fluoranthene			
2,4-Dinitrophenol	57	16	50	92	18	50
1,3,5-Trinitrobenzene	99.5	15	41	205.5	28	59
2,4,6-Trinitrochlorobenzene	54	18	54	121	18	46
2,4,6-Trinitrophenol	93.5	15	42	184.5	21	46
2,4,6-Trinitrotoluene	71	17	50	134	18	46
4-Nitrophthalic anhydride	102	21	57	131.5	18	46
Pyromellitic dianhydride	167	21	48	232	26	52
5-Nitrobenzofuroxan	—	(22)	(59)	92	29	80
4,6-Dinitrobenzofuroxan	82 93	1.1 12	3.1 33		decomp	
Benzotrifuroxan	83 86.5	5.0 1.3	14 3.6		decomp	
			Donor: Phenanthrene			
1,3,5-Trinitrobenzene	149.5	12	28	165.5	26	61
2,4,6-Trinitrophenol	78 107	4.6 13	13 33	147	22	53
2,4,6-Trinitrotoluene	—	(11)	(29)	100	28	75
4-Nitrophthalic anhydride	—	(14)	(37)	97.5	29	78
4,6-Dinitrobenzofuroxan	105.5 121	8.5 7.6	23 19		decomp	

a) Taken from Ref. 1. b) Taken from Ref. 3. c) The values are reproducible within 5% when the enthalpies are in the order of 10 kJ mol^{-1}. The errors are twice as large if the enthalpies are about 1 kJ mol^{-1}.

1, the thermodynamic data for the melting of these three complexes are for the stable forms. It is noteworthy that the entropy values of melting, 80 J mol^{-1} K^{-1} for the Fl–NBF, 75 J mol^{-1} K^{-1} for the Ph–TNT, and 78 J mol^{-1} K^{-1} for the Ph–NPA, are definitely larger than those of any other complexes in the table. The enthalpy and entropy associated with the monotropic transition given in Table 1 were estimated by taking the difference between the value for the melting of the stable form and that for the melting of the metastable form.

X-Ray Diffraction Patterns. In Fig. 2, the X-ray diffraction patterns observed at room temperature and above the transition temperature using filtered copper radiation are schematically presented for eight representative complexes. Reflecting the special natures of the donor and acceptor molecules, the room-temperature patterns are not simple and are markedly different from each other. However, the diffraction patterns are remarkably simplified upon the transition. Three or four lines are observable with the high-temperature forms: a strong line appearing between $2\theta_1=11$ and 12°, a weak one near $2\theta_2=20°$, and another strong one between $2\theta_4=26$ and 27°. The patterns of the Ph–TNP complex in its three forms were previously recorded by Koizumi and Matsunaga.[13] It was emphasized that the pattern given by the high-temperature form is very simple.

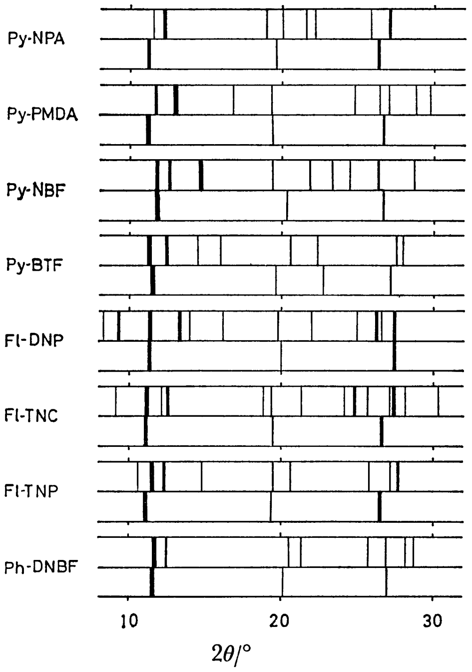

Fig. 2. X-Ray (Cu $K\alpha$ radiation) diffraction patterns of the molecular complexes. The upper pattern for each complex was recorded at room temperature and the lower one above the transition temperature.

Only three lines were found in it, in accordance with the present complexes. For some complexes, a very weak line is detectable near $2\theta_3=23°$, as is exemplified by the Py–BTF complex (see Fig. 2). The general features described here are in good agreement with those obtained for the six Py complexes studied before.

A comparison of the spacings, d_1, d_2, and d_3, which are inversely proportional to sin θ_1, sin θ_2, and sin θ_3 respectively, shows that

$$1/d_1:1/d_2:1/d_3 = 1:\sqrt{3}:2$$

within the limits of error of measurements, for all the complexes examined. On the other hand, the d_4 spacing is not in any simple ratio with the others. This remarkably simple ratio suggests that the lattice in the high-temperature form is hexagonal or trigonal.

With the hope of limiting further the probable structures, the density measurements were carried out for the Py–DNC, Py–DNT, Py–TNT, and Fl–TNC complexes, which can be transformed into the high-temperature forms below 60 °C. The densities measured within a few degrees below and above the transition temperature are summarized in Table 2. Trial shows that the trigonal lattice presented in Fig. 3 well explains the X-ray diffraction patterns and the observed densities and so seems probable. As this lattice must be common to all the complexes listed in Table 1, the shape of the component molecules is entirely ignored in this figure. The indices assigned to the above-mentioned four lines are (110), (300), (220), and (102). Table 2 records also the estimated unit-cell dimensions and the calculated densities. Three molecules of each component are in the cell shown in Fig. 3. The donor and acceptor molecules are stacked alternatively in infinite columns in parallel with the c-axis. The stacking angle may be nil, as the mean separation between the molecular planes is expected to be about 3.5 Å.

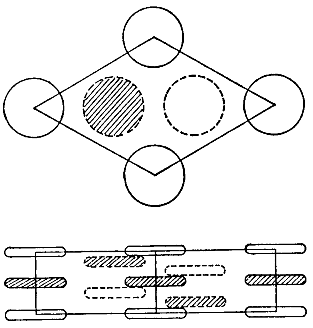

Fig. 3. Proposed structure for the isomorphous high-temperature forms. The molecules located at 000, 2/3 1/3 1/3, and 1/3 2/3 2/3 are different from those located at 0 0 1/2, 2/3 1/3 5/6, and 1/3 2/3 1/6.

Solid-solution Formation. The complete miscibility of a pair of the complexes is a severe test for the isomorphism. To be isomorphous, the high-temperature forms must have the same space group and the same number of molecules per unit cell.[14] The additional requirement to be miscible in all proportions is that the difference in the unit-cell sizes not be too great. The room-temperature forms of the Py–TNB and Py–TNP complexes have been reported to be isomorphous ($P\bar{1}$ and $Z=2$) by Herbstein and Kaftory.[2] Two enantiotropic transitions in the range from room temperature to the melting point are observed with both the complexes: 138 and 216 °C with the TNB complex and 164.5 and 178 °C with the TNP complex. The phase diagram of the pseudo-binary system comprising these two Py complexes given in Fig. 4 clearly shows that each pair of the polymorphs of these two complexes are completely miscible. The combination of the Fl–TNB and Fl–

Table 2. Densities measured within a few degrees below and above the transition temperature, and unit-cell dimensions and calculated density of the high-temperature form

Molecular complex	Density g cm^{-3}		Unit-cell dimensions		Calcd density g cm^{-3}
	Below Tp	Above Tp	a/Å	c/Å	
Py-DNC	1.414	1.396	15.31	6.99	1.42
Py-DNT	1.350	1.305	15.30	7.03	1.34
Py-TNT	1.450	1.415	15.84	7.03	1.40
Fl-TNC	1.506	1.449	15.80	6.94	1.49

TNP complexes gives similar results. The room-temperature forms are monoclinic ($P2_1/c$, $Z=4$), and the following unit-cell dimensions have been given by Herbstein and Kaftory: $a=8.48$, $b=7.27$, $c=30.35$ Å, $\beta=96°$ for the Fl–TNB complex, and $a=8.68$, $b=7.27$, $c=31.0$ Å, $\beta=96°$ for the Fl–TNP complex, fulfilling the conditions cited above.

The diagrams for the following six systems are illustrated in Fig. 5: Py–(NPA, DNF), Py–(DNF, TNT), (Py, Fl)–TNT, Fl–(TNT, TNP), (Fl, Ph)–TNP, and Ph–(TNP, TNB). These systems were selected so that the two molecular complexes share either a hydrocarbon or an acceptor. Moreover, the neighboring systems share one of the molecular complexes. In all the diagrams, the freezing points of mixtures lie between the melting points of the pure molecular complexes. These results undoubtedly indicate that the solid miscibility between the high-temperature forms is unlimited in all the systems shown in Fig. 5. Thus, we are quite certain that the high-temperature form of the Py–NPA is isomorphous with that of the Fl–TNT complex and also with that of the Ph–TNB complex. Besides the Fl–TNP complex described above, the room-temperature form of the Ph–TNB complex is known to be monoclinic ($P2_1/c$, $Z=4$), and that of the Ph–TNP complex, to be triclinic ($P1$ or $P\bar{1}$, $Z=2$).[2] Accordingly, a eutectoid system is produced by these two complexes, and the diagram is split by a miscibility gap at room temperature. It may be noticed from Fig. 5 that the formation of substitutional solid solutions based on the parent-complex lattices occurs extensively. The solubility of the Ph–TNP complex into the Ph–TNB complex lattice exceeds 60 mol%, while that in the inverse direction is merely about 20 mol%. The most striking example is found in the diagram involving the Fl–TNT and Fl–TNP complexes, which gives a peritectoid system. The Fl–TNT complex can dissolve the Fl–TNP complex over 80 mol%, and the width of the miscibility gap in this system is as narrow as 3 mol%.

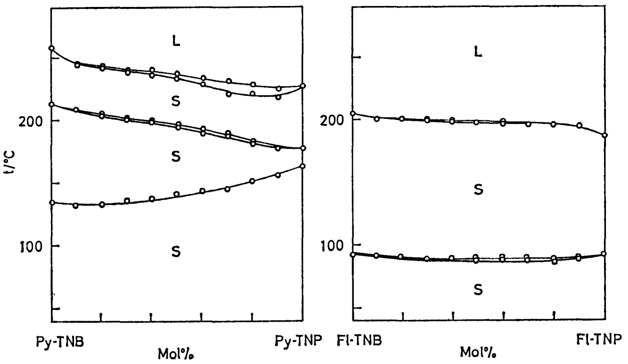

Fig. 4. Phase diagrams for the Py–(TNB, TNP) and Fl–(TNB, TNP) systems.

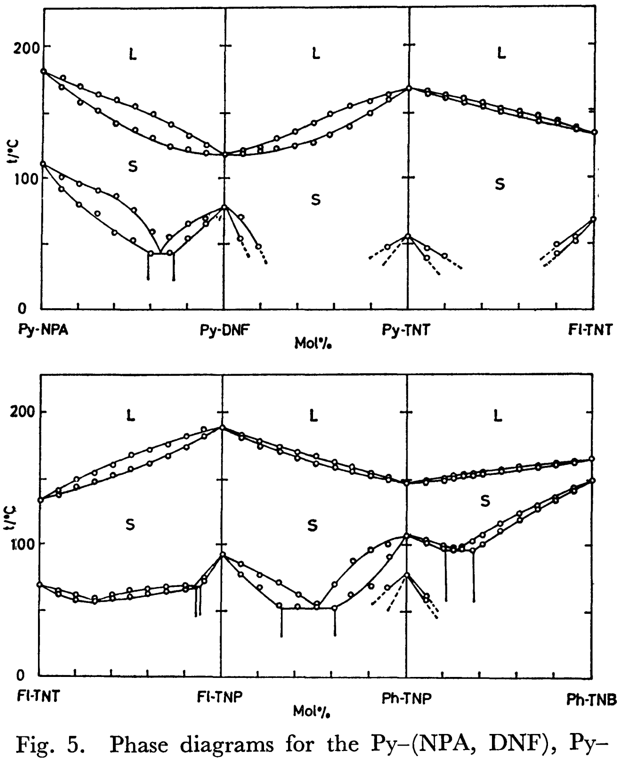

Fig. 5. Phase diagrams for the Py–(NPA, DNF), Py–(DNF, TNT), (Py, Fl)–TNT, Fl–(TNT, TNP), (Fl, Ph)–TNP, and Ph–(TNP, TNB) systems.

As the high-temperature forms of the Py–DNT and Fl–TNT complexes are isomorphous to each other, the pseudo-binary system gives a continuous solid solution (see Fig. 6). However, it must be noted that the composition of the solid solution is unusually different from the composition of the liquid solution in equilibrium. The equimolar mixture of these two complexes is equally considered to be an equimolar mixture of the Py–TNT and Fl–DNT complexes. As there is no unique high-temperature form appearing in the Fl–DNT complex, the miscibility gap should exist somewhere in the system consisting of the Py–TNT and Fl–DNT complexes. As expected, the diagram of the latter pseudo-binary system (shown in Fig. 6) has a gap extending from 60 to 90 mol% of the Fl–DNT complex. The large temperature difference between the solidus and liquidus near 50 mol% in the other pair of the complexes apparently arises from the wide miscibility gap located close to this composition. Results similar to those presented above may be anticipated for the system consisting of the Fl–TNT and Ph–TNP complexes because of the absence of a transition in the combination of Ph and TNT. Unexpectedly, however, the solidus and liquidus are not so separated as those in the system

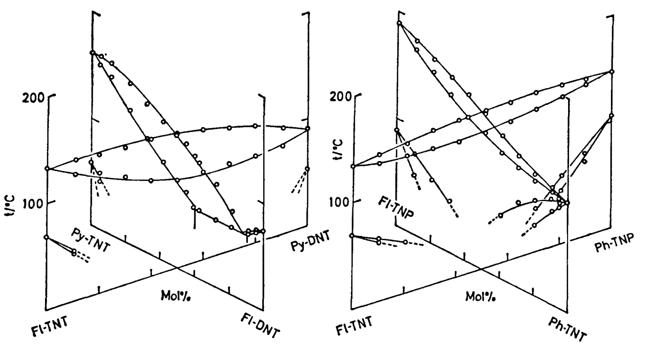

Fig. 6. Phase diagrams for the (Py, Fl)–(DNT, TNT) and (Fl, Ph)–(TNP, TNT) systems.

consisting of the Py–DNT and Fl–TNT complexes. The study of the system of the Fl–TNP and Ph–TNT complexes has revealed the formation of a continuous solid solution (see Fig. 6). The appearance of this phase must be due to the coincidence between the transition and melting points in the latter complex. The metastable polymorphs have also been found for the Fl–NBF and Ph–NPA complexes and have been demonstrated to be completely miscible at high temperatures with the Fl–TNT and Fl–NPA complex respectively (see Fig. 7).

Broad-line ^1H NMR. The second moment, the mean-square width of the resonance line, of the ^{1}H NMR spectrum is shown in Fig. 8 as a function of the temperature for each of the seven Py complexes. Py is known to have an intramolecular second moment of 3.43 G^2.[15] All the complexes studied here show evidence of molecular motion in the solid state, as indicated by a decrease in the moment. In the case of the TNB complex, the transition to the unique isomorphous form is located at 216 °C, well above the range measurable with our spectrometer. The second moment decreases gradually up to 138 °C and then more sharply above this temperature (see Fig. 8a). The value in the phase stable between 138 and 216 °C is as small as 1 G^2, indicating that some fast motional process exists before the transition to the isomorphous form. This observation is consistent with the small enthalpy and entropy values for the second transition. Similar small changes in the second moment are found for the TNP and DNBF complexes, in which the enthalpy and entropy of the transitions are also comparatively small. There is a large, abrupt drop in the second moment at the transition to the high-temperature forms of the other four complexes, reflecting a significantly larger enthalpy and entropy of the transition.

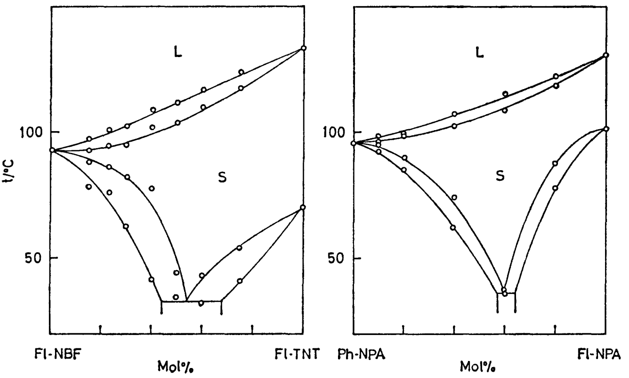

Fig. 7. Phase diagrams for the Fl–(NBF, TNT) and (Ph, Fl)–NPA systems.

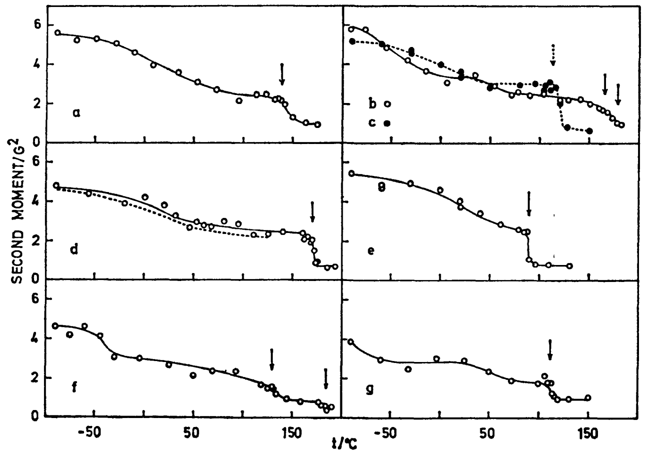

Fig. 8. Second moment values of the proton resonance for the pyrene complexes with a) TNB, b) TNP, c) NPA, d) PMDA, and the result by Fyfe (Ref. 15), e) NBF, f) DNBF, and g) BTF. The vertical arrows indicate the thermodynamic transition temperatures.

The PMDA complex is the only one among the complexes studied here for which the crystal structure has been determined. Herbstein and Snyman have made an intensive and comprehensive study of the structure at 110 and 300 K.[16] The NMR spectrum has been measured, and the nature of the molecular motions has been discussed by Fyfe.[15] Our results are essentially the same as his (see Fig. 8d). The moment observed at low temperatures compares very well with 4.8 G^2, the theoretical value for the rigid lattice calculated by means of Van Vleck's formula using the atomic coordinates of the X-ray determination. The reduction in the second moment to 2.3 G^2 by 130 °C has been interpreted by Fyfe in terms of the complete reorientation of the hydrocarbon molecules in their molecular planes. Furthermore, Dunn *et al.* have reported on heat-capacity measurements in the range from 10 to 323 K and have established the growth of orientational disorder over a very considerable temperature range.[17] Unfortunately, the transition located at 170 °C was covered by neither of these works.

Figure 9 shows the second moments of the nine Fl complexes. The intramolecular moment is esti-

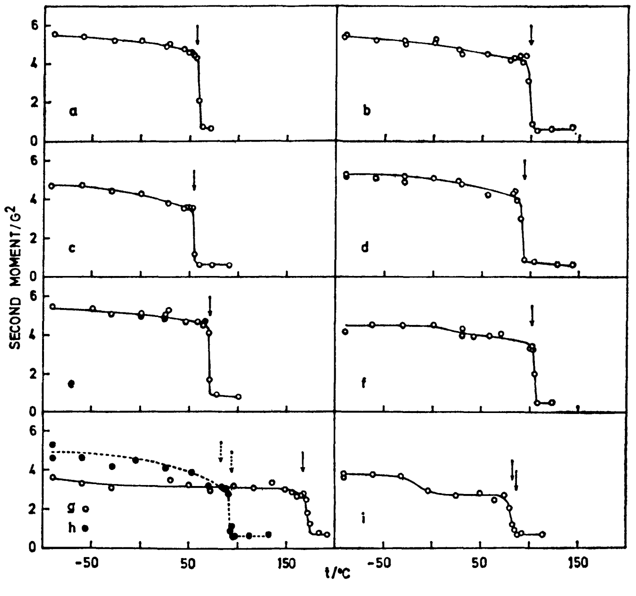

Fig. 9. Second moment values of the proton resonance for the fluoranthene complexes with a) DNP, b) TNB, c) TNC, d) TNP, e) TNT, f) NPA, g) PMDA, h) DNBF, and i) BTF. The vertical arrows indicate the thermodynamic transition temperatures.

mated to be 2.88 G^2 using the atomic coordinates previously reported by Herbstein and Kaftory.[2)] The change upon the transition into the isomorphous high-temperature form is drastic except for the BTF complex. In this complex, the reduction occurs by the transition at 83 °C rather than by that at 86.5 °C. The fact that the enthalpy of the former transition is about four times that of the latter may account for this result. The moment is generally not very temperature-dependent below the transition. There is no distinct reduction in the second moment by passing through the transition at 82 °C in the DNBF complex (see Fig. 9h).

The temperature variation in the second moment in the three Ph complexes is shown in Fig. 10. The moment drops abruptly and substantially upon the transition into the isomorphous form, but gradually at the other transitions in the TNP and DNBF complexes. Thus, the thermodynamic transition to the isomorphous form is, in general, accompanied by the abrupt reduction of the second moment. Such a coincidence implies that the molecules are moving fast on an NMR time-scale (40 MHz) above the transition temperature. Although the transition at 105.5 °C in the DNBF complex has a larger enthalpy than that at 121 °C, the change in the second moment is smaller and more gradual, suggesting that the motion initiated by the transition at 105.5 °C is not fast on an NMR time-scale. While the intramolecular moment of the hydrocarbon is calculated to be 4.12 G^2 on the basis of the molecular structure determined by Trotter,[18)] the observed moment in the isomorphous form is less than 1 G^2 in every complex. Therefore, the flat hydrocarbon molecules in this phase seem to have a considerable freedom of rotation. The large entropy associated with the transition supports also the onset of such a large degree of molecular motion.

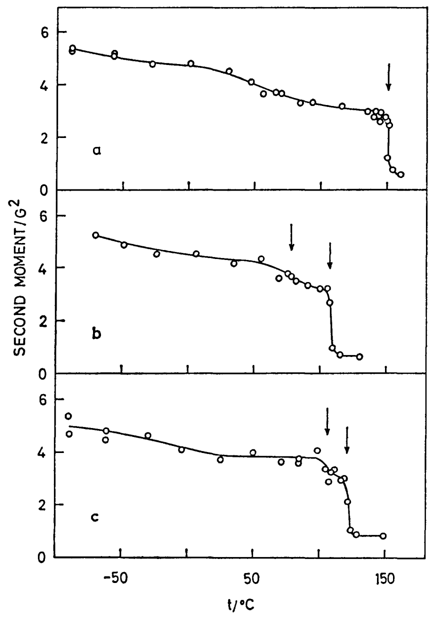

Fig. 10. Second moment values of the proton resonance for the phenanthrene complexes with a) TNB, b) TNP, and c) DNBF. The vertical arrows indicate the thermodynamic transition temperatures.

Benzene is an example which shows line narrowing due to rotation about a single axis.[19)] The second moment has been reported to show a slow decrease beginning at about 100 K and ending at about 120 K. Above this temperature, the moment is 0.76 G^2. The entropy of melting is 35.3 J mol^{-1} K^{-1}.[20)] Twice this value may be compared with those of our complexes: 46—67 J mol^{-1} K^{-1}. One should remember that this quantity is a measure of the difference in organization between the solid and the melt. As the association of the hydrocarbon and acceptor molecules is likely in the molten complexes,[21)] one cannot conclude, on the basis of these entropies, that the acceptor molecules are also mobile in the high-temperature forms. At any rate, the number of hydrogen atoms on the acceptor molecules is so small that the contribution to the second moment may be expected to be appreciably smaller than that due to the hydrocarbon molecules.

General Remarks. The molecular rotation certainly forms an important part of the mechanism for isomorphism reported here. In this connection, the present complexes bear some similarity to plastic crystals, which are composed of globularly shaped molecules. Plastic crystals are of a cubic habit. The transition entropy to this phase is high (about 40 J mol^{-1} K^{-1}) compared with that for melting (less than 20 J mol^{-1} K^{-1}). The largest transition entropy in our complexes to be compared is 59/2 J mol^{-1} K^{-1} for the metastable form of the Fl–NBF complex, while the largest entropy of melting is 67/2 J mol^{-1} K^{-1} for the Py–TNB complex. Clearly, the motion of the flat component molecules in the present complexes is generally more restricted than that of the spherical molecules in plastic crystals; nevertheless, some translational disorder might be also conceivable for the former crystals such as has been reported for the latter.[22)] The reactivity for donor- or acceptor-exchange in solids is currently under investigation below and above the transition temperature in order to search for such indications.

The sections of the van der Waals repulsion envelopes of the Py and Fl molecules are drawn in Fig. 11 as Al-Mahdi and Ubbelohde did for a number of aromatic molecules.[23)] The two are found to be sufficiently similar and to fit in essentially the same circle. The envelope of the Ph molecule is, of course,

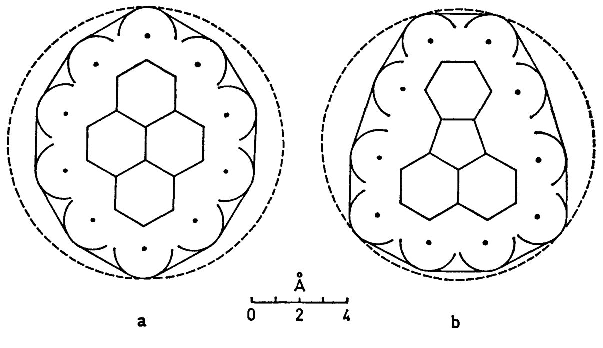

Fig. 11. Sections of van der Waals repulsion envelopes of the pyrene and fluoranthene molecules.

not very different from that of the Py molecule, but of a lower symmetry. If the molecules are rotating in their planes, the columns in the solid complexes of these three hydrocarbons would have cross sections very much alike and would produce unit-cell dimensions close to one another. The ease of the rotation seems to depend on comparatively small differences in the structure of the component molecules. The results summarized in Fig. 1 indicate that the rotation occurs most easily for the Py molecule with a higher symmetry and a little bit less easily for the Fl molecule. In the case of the Ph molecule, the shape of which is farther from a circle than the other two, the rotation is allowed only in limited complexes.

It is apparent that the lattice symmetry proposed in Fig. 3 is incompatible with the symmetry of the constituent molecules. This discrepancy provides one of the reasons for concluding that the molecules, even if not literally rotating, are disordered in orientation. The trigonal lattice is not entirely new for molecular complexes. Some years ago, Dahl found that the crystals of the hexamethylbenzene–hexafluorobenzene (1:1) complex are trigonal ($R\bar{3}m$) at room temperature and are transformed into a triclinic form ($P\bar{1}$) when cooled below 0 °C.[24,25] The lattice constants for the former form are $a=14.596\pm0.012$ Å and $c=7.124\pm0.007$ Å, fairly close to those given in Table 2. The donor and acceptor molecules are stacked alternatively in columns, with some disorder in the stacking sequence, in the trigonal form. No indication has been noted of such a disorder in the low-temperature form.[25] On the basis of thermal-vibration ellipsoids, Dahl postulated that rotation occurs for the hexamethylbenzene molecule not only in the trigonal form, but also in the triclinic form. We have examined the ^{1}H and ^{19}F NMR spectra of this complex. The second moment in the former spectrum is 11.3 G^2 at −142 °C and gradually decreases to 1.8 G^2 by −65 °C. Similarly, the moment in the latter spectrum shows a decrease from 1.2 to 0.65 G^2 in the same temperature range. The enthalpy associated with the transition located at about −25 °C is as small as 0.7 kJ mol^{-1}; therefore, no change in the second moment may be expected upon this transition.

The proposed lattice suggests that the stacking column acquires an effectively circular cylindrical symmetry. As the minimum distance between the sites for donor and acceptor molecules located in neighboring columns is less than the average of two molecular diameters, the molecules have no room to rotate freely and a change in the orientation requires correlated movements of interlocking molecules. For example, the distance is about 8.9 Å, and the average molecular diameter is about 10.6 Å, in the Py–DNC complex. The ratio of these two quantities, 0.84, fits nicely into the range of the minimum distance between molecular centers divided by the maximum diameter of the molecule, which is found for plastic crystals consisting of globular molecules, 0.81—0.94.[26]

In conclusion, it may be added that the electron acceptors in our complexes are relatively weak ones. The complexes are yellow to orange, and the mean separations between molecular planes are comparatively large, about 3.5 Å. Attempts to find isomorphous high-temperature forms with deeply colored complexes have not met with any success.

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