Isomorphism in the High-temperature Forms of the Pyrene Complexes with Five Polynitro Aromatic Compounds

Nobuaki Inoué* and Yoshio Matsunaga**
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received June 28, 1977)

Crystalline pyrene complexes with 2,4-dinitrofluorobenzene, 2,4-dinitrochlorobenzene, 2,4-dinitrotoluene, 2,4-dinitrophenol, and picryl chloride exhibit polymorphic transitions. Their temperatures and associated enthalpies are presented. The high-temperature forms show essentially identical X-ray diffraction patterns, losing the special natures of the substituents on the acceptor molecules. Isomorphism is supported by the formation of complete solid solutions demonstrated for combinations of these forms. The enthalpy and entropy of melting of the present complexes are characterized by rather small values, 4—6 kcal mol^{-1} and 12—14 cal deg^{-1} mol^{-1} respectively, indicative of anomalously high thermal motion or disorder in the high-temperature forms. Marked changes in the spectral and electrical properties by the transitions are noted in some cases.

The discovery of polymorphic forms has been reported for a number of electron-donor-acceptor complexes; however, little attention has been paid to their structure or to the properties expected to vary with the transitions.[1—12] In order to understand the significance of polymorphism, systematic studies of this phenomenon and of the change in physical properties by the transitions seemed to be highly desirable. For such studies, polymorphism should be observed with complexes consisting of component compounds structurally related to each other. Our preliminary survey indicated that pyrene complexes with polynitro aromatic compounds suit this purpose well. Especially, the five complexes studied here were found to be of considerable interest because of the isomorphism observed with the high-temperature forms.

Experimental

Materials. The pyrene, Eastman yellow label, was boiled with a large excess of maleic anhydride in xylene to remove the tetracene and other reactive impurities.[13] Then, the hydrocarbon was purified by chromatography on a column of activated alumina and finally zone-refined. The acceptors employed were 2,4-dinitrofluorobenzene (hereafter abbreviated as DNF), 2,4-dinitrochlorobenzene (DNC), 2,4-dinitrotoluene (DNT), 2,4-dinitrophenol (DNP), and picryl chloride (2,4,6-trinitrochlorobenzene) (TNC). They were obtained from commercial sources. The complexes were crystallized from benzene or chloroform solutions containing equimolar amounts of the component compounds. The melting points, listed in Table 1, are in fair agreement with the values reported by Shinomiya when available.[14]

Measurements. Calorimetric curves up to the melting points were recorded on a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 3 °C min^{-1}. The enthalpies of transition and of melting were estimated by comparing the peak areas with the enthalpy of the melting of naphthalene, 4.536 kcal mol^{-1},[15] and also with the enthalpy of transition in hexamethylbenzene, 0.422 kcal mol^{-1}.[16] X-Ray measurements on powdered samples were made with a Toshiba recording diffractometer, Model ADG 301, using filtered copper radiation. The sample was mounted on a aluminum plate with a 20-W heater attached to the other side. The temperature of this plate was monitored by means of a copper-constantan thermocouple and was kept constant with the aid of a Chino temperature-indicating controller, Type E 500.

For spectroscopic measurements, the complexes were melted between two quartz plates. Thin polycrystalline films were obtained by the repeated rubbing of two plates over one another, yielding an optical density of less than 1.0 throughout the visible region. The spectra were recorded on a Beckman DK 2A spectrophotometer at various temperatures between 20 and 80 °C with the aid of a temperature-regulated cell holder. Electrical resistivity measurements were performed on pressed pellets by the two-probe method, as has been described in a paper by Koizumi and Matsunaga.[8]

Results and Discussion

The transition temperature, enthalpy, and entropy are collected in Table 1. Fortunately, the transitions in these complexes occur at reasonably low temperatures and are well separated from the melting points. These conditions make our studies of the high-temperature forms considerably easy. The enthalpy of transition is about 3 kcal mol^{-1} or more in all the complexes but that with DNC. When the high-temperature forms of the DNF, DNT, and DNP complexes are quickly cooled, the metastable phases may be obtained, as evidenced by new transitions appearing at 53, 33, and 39 °C respectively.

The X-ray diffraction patterns observed at room temperature are complicated and distinctly different from each other, reflecting the special natures of the substituents. However, the patterns are drastically simplified upon the transition and become almost identical in all five. As is schematically illustrated in Fig. 1, only four diffraction lines can be seen in the range examined: a strong one appearing between 11 and 12°, two weak ones near 20 and 23°, and a strong one between 26 and 27°. If these high-temperature forms really have the same space group and number of molecules per unit cell, a combination of any two should give a continuous solid solution.[17] Moreover, the combinations examined so far consist of molecular complexes sharing the same acceptor compound.[8,18—20] On the other hand, all the present complexes share the same donor compound, pyrene. Consequently, we decided to look into phase diagrams for several selected pairs by means of differential scanning calorimetry. In addition, the phase boundaries at

---

* Present address: Fuji Photofilm Co., Minami-ashigara, Kanagawa.
** To whom inquiries may be addressed.

Table 1. Thermodynamic data of pyrene complexes with polynitro aromatic compounds

Acceptor	Transition			Melting		
	t/°C	ΔH/kcal mol^{-1}	ΔS/e. u.	t/°C	ΔH/kcal mol^{-1}	ΔS/e. u.
2,4-Dinitrofluorobenzene	76.5	4.3	12	119	5.0	13
2,4-Dinitrochlorobenzene	41	0.57	1.8	87	4.2	12
2,4-Dinitrotoluene	53.5	2.9	8.9	92.5$^{a)}$	4.8	13
2,4-Dinitrophenol	53	3.1	9.5	144$^{b)}$	5.9	14
Picryl chloride	79$^{c)}$	3.2	9.1	154.5$^{d)}$	5.2	12

a) 92.5 °C by Shinomiya (Ref. 14). b) 146.3 °C (Ref. 14). c) 81 °C by Bando and Matsunaga (Ref. 12). d) 154 °C (Ref. 14).

room temperature were checked by the examination of the X-ray diffraction patterns. For example, the diagrams for the following three systems are presented in Fig. 2: pyrene–(DNP,DNC), pyrene–(DNC,DNT), and pyrene–(DNT,DNP). The composition is quoted in the mole percentage of the acceptor. The solid-liquid equilibria are of the I type in the Roozeboom classification and clearly indicate the formation of a continuous solid solution within the temperature limits of the diagrams.[21] Similar equilibria have also been noted in pyrene–(DNC,DNF), pyrene–(DNF,DNT), and pyrene–(DNT,TNC). Thus, isomorphism in the high-temperature forms of the five complexes is firmly established.

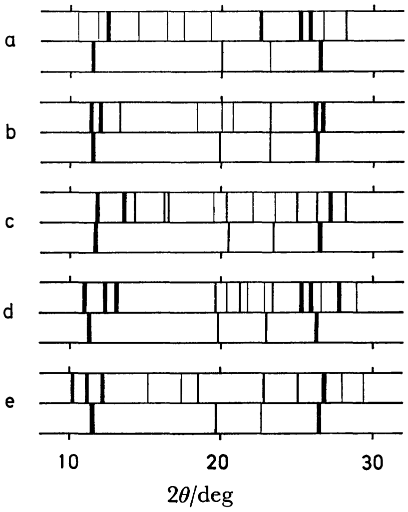
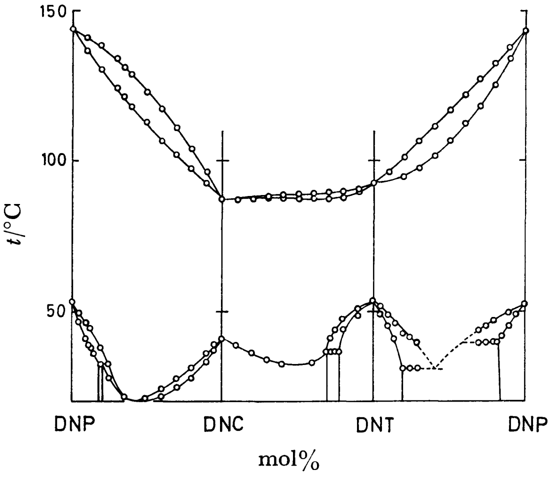


Fig. 1. X-Ray diffraction patterns of the pyrene complexes with a) DNF, b) DNC, c) DNT, d) DNP, and e) TNC. The upper pattern for each complex was recorded at room temperature, and the lower one above the transition temperature.



Figs. 2. Phase diagrams for the pyrene–(DNP, DNC), pyrene–(DNC, DNT), and pyrene–(DNT, DNP) systems.

The solubility characteristics of the low-temperature forms in pyrene–(DNP,DNC) and pyrene–(DNC, DNT) bear a similarity to each other. They are all peritectoid systems. The formation of substitutional solid solutions based on the parent complex lattices occurs over a wide range of stoichiometry. Both the transition temperatures are appreciably lowered by the formation of solid solutions. It is interesting to note that the solubility of the DNP complex into the DNC complex lattice is as much as 80 mol%. Therefore, a miscibility gap with a width as narrow as 2 mol% appears in this system. Similarly, the DNC complex can dissolve the DNT complex to an extent of 70 mol%. The width of the miscibility gap in pyrene–(DNC, DNT) is about 8 mol%.

The diagram for pyrene–(DNT,DNP) could be only partially determined because samples in the range from 30 to 70 mol% of DNP were found not in equilibrium even after standing over two years at room temperature. Nevertheless, the presence of two singular points may be easily noted. As is shown in Fig. 2, one of them may be a eutectoid at about 40 mol% and at 31 °C, while the other may be a peritectoid at about 60 mol% and at 40 °C. If this assignment is correct, and if the equilibrium is achieved, the appearance of a ternary complex dissolving adjacent phases to some extent, and hence of a variable composition, may be expected. This phase may cover a range as wide as 20 mol% of DNP. The formation of two ternary complexes has been known in the (phenanthrene, anthracene)–picric acid system studied by us.[8] They may be supposed to be deposited from mixtures containing liquid phases. In the case of pyrene–(DNT, DNP), the ternary complex must be formed from a solid solution. In other words, an extensive rearrangement of the component molecules must occur in the solid state for the appearance of the new phase. Such a process undoubtedly takes a long time to be accomplished. The other, but less likely, possibility is that the above-mentioned singular points are both eutectoids. If so, the miscibility gap for the high-temperature forms is closed at these points, while that for the low-temperature forms covers the whole range from 20 to 84 mol% of DNP.

Although our knowledge of the structural relationship among various molecular complexes is still scanty, several isomorphous pairs are already known. For example, the trinitrobenzene and picric acid complexes of naphthalene, fluoranthene, and pyrene have each been shown to be strictly isomorphous by Herbstein and Kaftory.[9] This relationship has been established for the crystals stable at room temperature. Our results strongly suggest that, if high-temperature forms are examined, isomorphism in molecular complexes may be observed more commonly than has been supposed.

When the interaction between the hydrocarbon molecule and the substituent on the acceptor molecule is specific or localized, the lattice may be rather rigid. The disappearance of this specific interaction above the transition temperature may be due to the onset of an anomalously great thermal motion of the component molecules. This motion appears so great that the interaction is dynamically averaged and becomes nonspecific. Such a thermal motion is expected to contribute significantly to the melting mechanism of the complexes. This speculation is supported by our observation that the enthalpy and entropy of melting of the present complexes are only 4—6 kcal mol^{-1} and 12—14 cal deg^{-1} mol^{-1} respectively (see Table 1). These values are definitely small if compared with the data for the eleven polycyclic aromatic hydrocarbon-trinitrobenzene complexes given by Casellato *et al.*[11] The enthalpy ranges from 6.5 kcal mol^{-1} for the phenanthrene complex to 14.5 kcal mol^{-1} for the dibenzoanthracene complex. The corresponding entropies are 14.9 and 28.5 cal deg^{-1} mol^{-1} respectively. The former complex is known to exhibit a polymorphic transition at 148 °C with an enthalpy value of about 3 kcal mol^{-1}. Apart from this, only the pyrene complex has an entropy value below 20 cal deg^{-1} mol^{-1}. The observed entropies can probably be divided unevenly among the donor and acceptor lattices. On the basis of the wide-line NMR measurements, the reorientation of the donor species in a number of molecular complexes has been suggested by Fyfe and others. It may be added that pyrene and its complexes are notable of this examples.[22—24] The present complexes are now being examined by this technique in our laboratory. The second moments are reduced to 1—2 G^2 at the transition temperatures in all the complexes.

Not only the mode of interaction between the donor and acceptor molecules, but also that between like molecules in a complex may be modified by the structural change upon the polymorphic transition. The charge-transfer absorption has a direct bearing upon the former interaction, and the electrical resistivity, upon the latter. Their temperature dependences may each show anomalies at the transition temperature; however, the magnitudes may be quite different. Consequently, studies of these two properties in parallel may be fruitful. As the only discernible change in the charge-transfer absorption was the intensification upon the transition, the optical density at the absorption maximum is plotted against the temperature in Fig. 3. The value of the low-temperature form was arbitrarily taken as 1.00 in this figure. The most pronounced change is found with the DNT complex. The optical density at 413 nm after the transition is as much as 4.25 times that before. After the transition, the optical density increases linearly with the temperature, the value at 74 °C being 4.80. The other extreme is observed with the DNC complex, which is known to show the smallest enthalpy of transition. The optical density remains constant throughout the transition. Although the other three complexes show large enthalpy changes upon the polymorphic transition, the increase in the optical density is only about 10% or less.

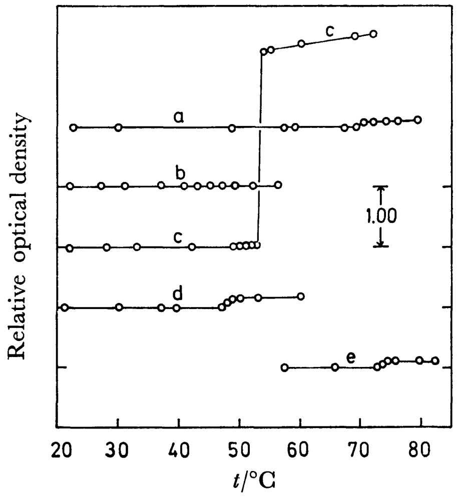


Fig. 3. Temperature dependence of the relative optical density of charge-transfer absorption in the pyrene complexes with a) DNF (at 390 nm), b) DNC (at 400 nm), c) DNT (at 413 nm), d) DNP (at 440 nm), and e) TNC (at 425 nm).

In Fig. 4, the variation in the electrical resistivity recorded at ascending temperatures is presented. The magnitude of resistivity varies greatly among the members of the series. Thus, the DNF complex is more conducting than TNC complex by a factor of 10^3. All the complexes exhibit abrupt decreases in the resistivities at the transition temperatures. Here again, the change observed with the DNT complex is the largest. Therefore, one may postulate that the donor-donor and/or acceptor-acceptor overlaps are considerably improved by the structural change, as is the overlap between the hydrocarbon and DNT molecules. The DNP complex shows a decrease in the resistivity by almost the same factor. In this case, like molecules presumably gain better overlaps by the transition, without any appreciable effect on the donor-acceptor interaction. It is interesting to point out that, in spite of having the largest enthalpy of transition, the DNF complex exhibits a decrease by merely a factor of five, and that this factor can be well compared with that observed with the DNC complex. The latter is the one with the smallest enthalpy of transition among the complexes studied here. However, we must be aware of a large difference in the magnitude of resis-

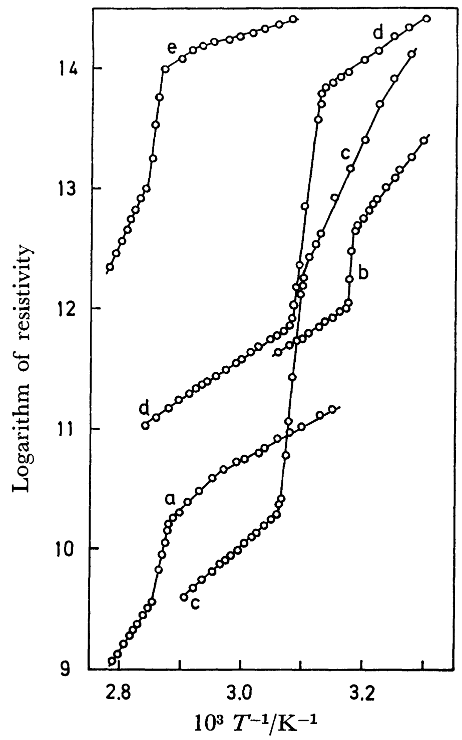


Fig. 4. Electrical resistivities of the pyrene complexes with a) DNF, b) DNC, c) DNT, d) DNP, and e) TNC.

tivity between these two. Since the DNF complex has a relatively low resistivity, the improvement of the overlap between like molecules in this complex cannot be compared with that of the DNC complex by such a factor. If one refers to the magnitude, it is certain that the resistivity change is particularly large for the DNF complex. The acceptor, TNC, is undoubtedly the strongest employed here; nevertheless, its pyrene complex is the least conducting one. The crowded substituents on this acceptor molecule seem to prevent good overlaps between like molecules in this complex. At descending temperatures, large hystereses were observed in all the cases because of a considerable delay in the transition in the reverse direction.

The authors wish to express their thanks to Professor Toshio Yokokawa for letting them use the X-ray diffractometer.

References

1) A. Kofler, *Z. Elektrochem.*, **50**, 200 (1944).
2) D. E. Laskowski, D. G. Grabar, and W. C. McCrone, *Anal. Chem.*, **25**, 1400 (1953).
3) H. Matsuda, K. Osaki, and I. Nitta, *Bull. Chem. Soc. Jpn.*, **31**, 611 (1958).
4) T. Sakurai, *Acta Crystallogr.*, **19**, 320 (1965).
5) Y. Matsunaga, *Nature*, **211**, 183 (1966).
6) Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **44**, 2868 (1971).
7) F. Pelizza, F. Casellato, and A. Girelli, *Thermochim. Acta*, **4**, 135 (1972).
8) S. Koizumi and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **47**, 9 (1974).
9) F. M. Herbstein and M. Kaftory, *Acta Crystallogr., Sect. B*, **31**, 60 (1975).
10) Y. Matsunaga, E. Osawa, and R. Osawa, *Bull. Chem. Soc. Jpn.*, **48**, 37 (1975).
11) F. Casellato, C. Vecchi, and A. Girelli, *Thermochim. Acta*, **13**, 37 (1975).
12) M. Bando and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **49**, 3345 (1976).
13) E. Clar, *Ber.*, **69**, 1683 (1936).
14) C. Shinomiya, *Bull. Chem. Soc. Jpn.*, **15**, 259 (1940).
15) J. P. McCullough, H. L. Finke, J. F. Messerly, S. S. Todd, T. C. Kincheloe, and G. Waddington, *J. Phys. Chem.*, **61**, 1105 (1957).
16) M. E. Spaght, S. B. Thomas, and G. S. Parks, *J. Phys. Chem.*, **36**, 882 (1932).
17) A. I. Kitaigorodskii, "Organic Chemical Crystallography," Consultants Bureau, New York (1961), p. 231.
18) H. Rheinboldt and P. Senise, *Bols. faculdade filosofia, cienc. letras. Univ. São Paulo*, **14**, *Quimica* No. 1, 3 (1942), as cited in *Chem. Abstr.*, **40**, 2049 (1946).
19) S. K. Lower, *Mol. Cryst. Liq. Cryst.*, **5**, 363 (1969).
20) S. Koizumi and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **46**, 1875 (1973).
21) H. W. B. Roozeboom, *Z. Phys. Chem.*, **30**, 385 (1899).
22) C. A. Fyfe, D. F. R. Gilson, and K. H. Thompson, *Chem. Phys. Lett.*, **5**, 215 (1970).
23) C. A. Fyfe, *J. Chem. Soc. Faraday Trans. 2*, **70**, 1633 (1974).
24) C. A. Fyfe, D. Harold-Smith, and J. Ripmeester, *J. Chem. Soc. Faraday Trans. 2*, **72**, 2269 (1976).