BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1875—1876 (1973)

Phase Diagram of the Phenanthrene/Carbazole-Picric Acid System

Shigeo Koizumi* and Yoshio Matsunaga**

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received October 20, 1972)

By means of differential scanning calorimetry, it has been found that phenanthrene picrate exhibits an enantiotropic transition at 77 °C in addition to the one at 106 °C reported by Kofler.[1,2] The recovery of the low-temperature form is so slow that the newly-found transition cannot be observed in the second run if it is examined immediately after the first heating. Furthermore, the addition of anthracene, a major impurity in phenanthrene, has been found to slow down the recovery. As carbazole is another major impurity in phenanthrene, an examination of the phenanthrene/carbazole picrate seemed to be desirable in order to confirm the effects of impurities on the above-mentioned phase-transition.

Phenanthrene, Eastman white label, was purified according to the method reported by Feldman *et al.*,[3] and then by zone-refining. After these processes, the content of anthracene was estimated to be less than 10^{-4} mol%, because the electronic absorption maximum located at 376 nm characteristic of anthracene was no longer detectable in a cyclohexane solution. Carbazole from the Koso Chemical Co. was refluxed with acrylonitrile in toluene for ten hours to remove the anthracene, and was then recrystallized twice from benzene. Picric acid, Wako special reagent grade, was purified by recrystallization from ethanol. The picrates were crystallized from methanol containing equimolar amounts of the component compounds. Although mutual solid solubility in many pairs of molecular complexes has been examined by Rheinboldt and Senise[4] and by Lower,[5] phenanthrene/anthracene-*s*-trinitrobenzene is the only system for which a phase diagram has been described in detail. Consequently, we decided to look into the whole system rather than just the phenanthrene-rich region. Samples were prepared by melting powdered mixtures with known ratios of the parent complexes. The composition is quoted in the mole percentage of the carbazole. After storage at room temperature for a week, the melting points and transition temperatures were determined using a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, at a heating rate of 3 °C/min. X-Ray measurements on powdered samples were made at room temperature with a Toshiba recording diffractometer, Model ADG-301, using filtered copper radiation.

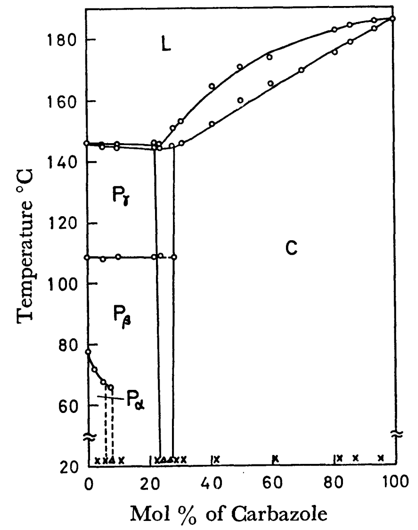

Fig. 1. The phenanthrene/carbazole-picric acid phase diagram.
○: calorimetric points, ×: single phase by X-ray diffraction, △: two phases by X-ray diffraction.

The experimental points determined by calorimetry are plotted in Fig. 1. This diagram is of the same type as that of the phenanthrene/anthracene-*s*-trinitrobenzene reported by Lower,[5] and shows the formation of two series of solid solutions, P and C, based on the two parent complex lattices, which have not previously been known. A eutectic occurs at about 24 mol% carbazole and at 145 °C. This temperature is nearly the same as the melting point of pure phenanthrene picrate. Therefore, the solidus and liquidus are almost flat and coincide with each other in the phenanthrene-rich region. The first phase-transition in the phenanthrene picrate is markedly lowered by the addition of small amounts of the carbazole picrate; *e.g.*, it becomes 66 °C at 6.86 mol%. Above this composition, the $P_\alpha \rightarrow P_\beta$ transition could not be detected by calorimetry. This result is similar to that reported for the phenanthrene/anthracene picrate.[1] Therefore, it is certain that carbazole can affect the rate of recovery as much as anthracene does. The X-ray examination revealed that the solid solution containing 5.12 mol% carbazole is single-phase, while those containing 5.91 and 6.86 mol% are mixtures of the P_α and P_β terminal solid solutions, indicating that the equilibrium condition could not be established by one week's storage. If the solid solutions containing more carbazole could be well annealed, the phase boundary between P_α and P_β would extend to about 22 mol%. On the other hand, the second phase-transition temperature is essentially independent of the composition and is detectable as

---

* Present address: Fuji Photo-Film Co., Minami-ashigara, Kanagawa.

** To whom inquiries may be addressed.

[1] Y. Matsunaga, This Bulletin, **44**, 2868 (1971).

[2] A. Kofler, *Z. Elektrochem.*, **50**, 200 (1944).

[3] J. Feldman, P. Pantages, and M. Orchin, *J. Amer. Chem. Soc.*, **73**, 4341 (1951).

[4] H. Rheinboldt and P. Senise, *Bols. faculdade filosofia, cienc. letras, Univ. São Paulo*, **14**, *Quimica* No. 1, 3 (1942), through *Chem. Abstr.*, **40**, 2049 (1946).

[5] S. K. Lower, *Mol. Cryst. Liq. Cryst.*, **5**, 363 (1969).

far as 28 mol% carbazole. Above 26 mol%, the X-ray diffraction pattern recorded at room temperature is clearly that of the carbazole picrate, although the lattice constants increase more or less upon the addition of phenanthrene; *e.g.*, a diffraction peak located at 12.82° in the pure carbazole picrate moves to 12.30° at 30 mol% carbazole. This change corresponds to an increase of 0.30 Å in the distance of 6.91 Å in the pure carbazole picrate. The presence of a narrow miscibility gap, the width of which could be influenced by non-equilibrium effects, was confirmed by the X-ray data, as is indicated in Fig. 1.

The authors wish to express their thanks to Professor Toshio Yokokawa for letting them use the X-ray diffractometer and to Dr. Eiji Osawa for his advice concerning the purification of carbazole.