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Effects of Alkyl Chain Length on Molecular Interactions. I. Solid Complex Formation in the Pyrene–*N*-Alkyl-2,4,6-trinitroaniline Systems

Atsushi Togashi and Yoshio Matsunaga*
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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Phase diagrams were prepared for the fifteen binary systems consisting of pyrene as an electron donor and *N*-alkyl-2,4,6-trinitroanilines as electron acceptors. The thermal stability of the orange 1:1 complex between pyrene and the unsubstituted 2,4,6-trinitroaniline (mp 236 °C) is drastically decreased by *N*-alkylation; *e.g.*, the *N*-pentyl-2,4,6-trinitroaniline complex melts at 97 °C. The systems with the *N*-hexyl and *N*-heptyl derivatives give two peritectics each, while most of the higher homologues produce a single peritectic or a eutectic. Unstable red solids were formed on rapid cooling of the molten pyrene–*N*-hexyl-2,4,6-trinitroaniline mixtures. This red complex becomes relatively more stable with increase of the alkyl chain length, possibly because of the enhanced tendency for chain alignment. In the systems with the *N*-pentadecyl and *N*-heptadecyl derivatives, the stable existence of the red 1:1 complex could be demonstrated.

Many organic compounds that form liquid crystals when heated have elongated molecules. Generally, these molecules have a rigid central part and one or two flexible terminal groups. The effects of the alkyl chain length in the terminal substituents on the liquid crystalline properties have been studied for a large number of homologous series. The lower homologues are commonly purely nematic, whereas the higher homologues are purely smectic. The flexible terminal groups are supposed to bring about partial breakdown of the molecular order produced by the attraction between the rigid central parts. As the nematic phase is less ordered than the smectic phase, one might assume that shorter alkyl chains tend to diminish the thermal stability of the regular molecular arrangement, while longer ones tend to restore it though the arrangement achieved is not the same as the original one. If this is so, analogous effects would be widely observable with ordinary organic solids; however, little attention has been paid to this problem.

In the present series of communications, we record studies on the effects of the alkyl chain length on intermolecular interactions such as charge transfer and proton transfer operating in solid complex formation. Systematic studies may hopefully provide a way to control such interactions. As early as 1910, Sudborough and Beard reported the preparation of 1,3,5,-trinitrobenzene complexes with aminobenzoic acids and their methyl and ethyl esters.[1] The progressive lowering of their melting points in this order appears to be consistent with the above-mentioned trends. To the authors' knowledge, no further work on such solid complexes is available.

Experimental

Materials. The yellow-colored *N*-alkyl-2,4,6-trinitroanilines were obtained by the condensation of appropriate amines with 2,4,6-trinitrochlorobenzene in boiling ethanol.[2] The alkyl groups employed and the melting points of the products were as follows: butyl, 83.5 °C; pentyl, 73.5° C; hexyl, 70.2 °C; heptyl, 59.5 °C; octyl, 63.5 °C; nonyl, 55.6 °C; decyl, 70.2 °C; undecyl, 68.4 °C; dodecyl, 76.3 °C; tridecyl, 77.0 °C; tetradecyl, 79.0 °C; pentadecyl, 83.5C; hexadecyl, 88.3 °C; heptadecyl, 89.0 °C; octadecyl, 91.5 °C. The pyrene, Eastman white label, was recrystallized from xylene. Binary mixtures in known proportions were melted in small test tubes, shaken well to insure homogeneity and then rapidly cooled.

Measurements. The calorimetric curves were recorded on a Rigaku Denki Thermoflex differential scanning calorimeter during the process of heating. The heating rate in this work was generally 5 °C min^{-1} but a rate as high as 20 °C min^{-1} was occasionally employed for the determination of melting points of metastable forms. The binary mixture was put into an open aluminum pan so that the color change on heating could be observed through a window. The diffuse reflectance of the solid component compounds and the molecular complexes was measured with a Beckman DK 2A spectroreflectometer. The spectrum was then plotted using the Kubelka-Munk function.

Results and Discussion

Shinomiya has prepared the phase diagram of the pyrene–2,4,6-trinitroaline system.[3] The eutectic on the donor-rich side is located at 139.5 °C and 8 mol% (hereafter, the composition is given by mol% of the acceptor) and the other one at 180.5 °C and 88 mol%. The stable 1:1 complex melts at a temperature as high as 236 °C. When the *N*-butyl and *N*-pentyl derivatives are employed as electron acceptors, the diagrams are essentially of the same type; that is, the orange 1:1 complexes melt congruently (see Fig. 1a). However, the temperatures are lowered to 104.5 and 97 °C respectively.

As is evident from Fig. 1b, the 1:1 complex becomes so unstable for the *N*-hexyl derivative that it undergoes decomposition at 85.5 °C, exhibiting a peritectic point at 55 mol%. Thus, the decrease in the thermal stability of the orange 1:1 complex by the *N*-alkylation is remarkable. In this system, another peritectic is found at 97 °C and 37 mol%, suggesting the formation of a 2:1 complex. The latter is also orange-colored. In addition, red solids crystallize when the molten mixtures around this composition are quenched. The melting point of this metastable phase (68 °C) is measurable by a rapid heating (see the shaded circles in Fig. 1b) though these red solids change monotropically to orange solids on storage at room temperature. The endothermic peak due to the melting is followed by an exothermic peak and the stable orange-colored solid is formed. The pyrene–*N*-heptyl-2,4,6-trinitroaniline system behaves similarly; however, the stabilities of the complexes are further diminished. Namely, the peri-

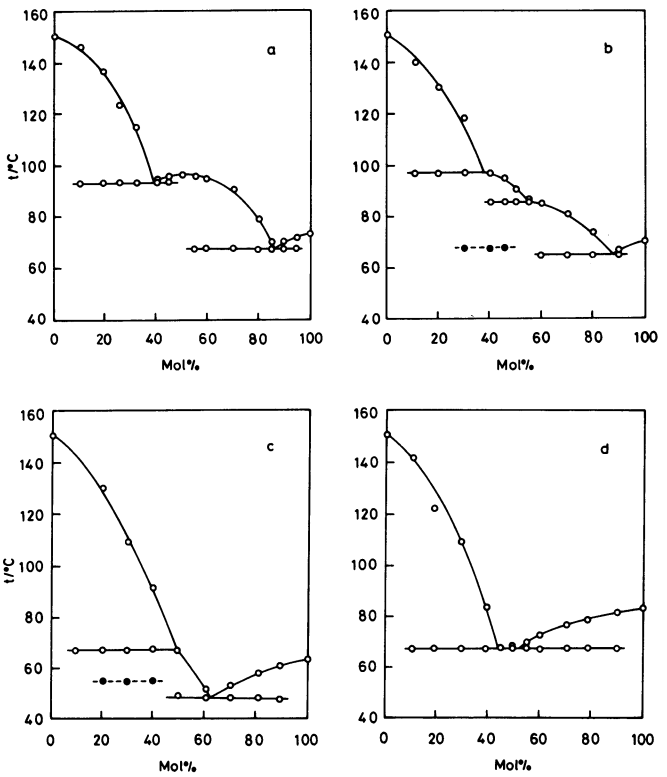

Fig. 1. Phase diagrams of the systems of pyrene with (a) *N*-pentyl-2,4,6-trinitroaniline, (b) the *N*-hexyl analogue, (c) the *N*-octyl analogue, and (d) the *N*-pentadecyl analogue. The shaded circles are the melting points of the metastable phase.

tectic due to the 1:1 complex is at 63 °C and 65 mol% and that due to the 2:1 complex at 85 °C and 38 mol%. In the composition range of the latter complex, a red complex melting at 61 °C is obtainable. The eutectic point of this system is located at 53 °C and 90 mol%.

The combination of pyrene and the *N*-octyl derivative exhibits only one peritectic at 67 °C and 48 mol%, giving no evidence for the formation of the 1:1 complex (see Fig. 1c). Metastable red solids appearing in the range from 20 to 40 mol% melt at 54.5 °C regardless of the composition. The phase diagrams of the same type were afforded by the next five higher homologues. In the case of the *N*-nonyl derivative, the system gives a peritectic at 71.5 °C and 49 mol% and a eutectic at 45.5 °C and 71 mol%. The latter temperature is the lowest among the eutectics observed in the present series. Moreover, it may be added that only in this system the red solids were so unstable that we failed to record the melting point on the calorimetric curve even with the highest rate of heating. With the *N*-decyl derivative, both the peritectic and eutectic raise appreciably; that is, the former lies at 90.5 °C and 42 mol% and the latter at 63 °C and 77 mol%. The melting point of the metastable red solid was determined as 60 °C. The peritectic and eutectic points fall again with the *N*-undecyl derivative. They are found at 76 °C and 46 mol% and at 59 °C and 73 mol%. As a result the red solids melt at 56.5 °C. The peritectic continues to fall with the *N*-dodecyl and *N*-tridecyl derivatives. They lie at 75.5 °C and 44 mol% and at 65 °C and 47 mol% respectively. On the other hand, the eutectic changes rather irregularly; that is, 64 °C and 65 mol% for the former homologue and 62.5 °C and 55 mol% for the latter. The melting point of the metastable red form shows a similar tendency to the eutectic; namely, 61.5 and 58.5 °C were recorded for these systems. Thus, the melting point of the red phase is not much affected by the alkyl chain length up to the *N*-tridecyl derivative; however, a rather large alternation in the thermal stability is demonstrated beyond this member in the series. Such an alternating effect is strongly reminiscent of the well-known alternation of the melting points of long chain compounds, which is attributed to the fact that the alkyl chains in the crystal lattice are in the form of long, straight but zig-zag chains and lie with their axes parallel.[4]

When molten mixtures of pyrene and *N*-tetradecyl-2,4,6-trinitroaniline are slowly cooled, no stable complex is found. The eutectic is located at 59 °C and 50 mol%, whereas the metastable red complex can be formed by rapid cooling in this system also. Its melting point is lower by 10 °C than the eutectic. The yellow solids exothermally produced above this melting point are mixtures of the component compounds. Therefore, the stability of the orange complex is now definitely lower than that of the red one though the latter is still metastable. The systems with the next two even-numbered homologues maintain a similar behavior. Each diagram shows only a eutectic point which is at 67.5 °C and 42 mol% and at 72 °C and 44 mol%. The red complex formed in the former system melts at 55.5 °C and that in the latter at 63.5 °C.

The systems with the *N*-pentadecyl and *N*-heptadecyl derivatives are of particular interest because in them the stable existence of the red complexes could be demonstrated. As is shown in Fig. 1d, the freezing point curve of the hydrocarbon meets a horizontal line at 68 °C and 44 mol% and that of the *N*-pentadecyl derivative at the same temperature and 53 mol%. Although the equilibrium curve involving the congruently-melting red complex is not distinguishable from the eutectic horizontal, the composition range strongly suggests that the ideal mole ratio of this phase is 1:1. In the case of the *N*-heptadecyl derivative, the binary system is somewhat complicated and has a peritectic point at 72.5 °C and 47 mol%, supporting the formation of a 1:1 complex. The eutectic point lies at 71 °C and 40 mol%. Occasionally, we obtained yellow mixtures of the solid component compounds from the melts of this system. Upon heating, this yellow mass melts but immediately solidifies into the red complex. This change is accompanied by evolution of heat.

The thermal stabilities are plotted against chain length in Fig. 2 for the above-mentioned three kinds of molecular complexes. Open circles represent the congruent or incongruent melting points of the orange 1:1 complexes. The stability diminishes rapidly with increase in the alkyl chain length and this complex can be found only in the region I which extends up to the *N*-heptyl derivative. In view of the enhanced flexing of the alkyl chains, the lowering of melting point in this region is reasonable. The metastable red complex

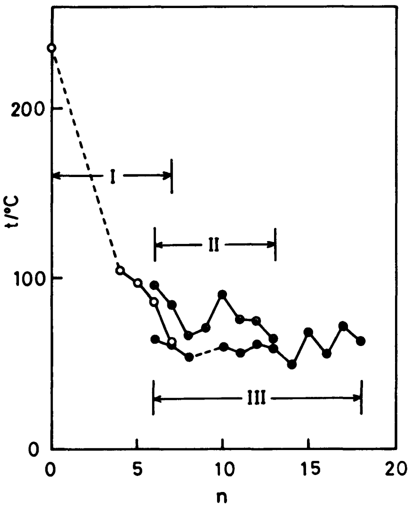

Fig. 2. Congruent or incongruent melting points of the orange-colored 1:1 complex (○), of the orange-colored 2:1 complex (⊙), and of the red-colored 1:1 complex (●) plotted against the N-alkyl chain length.

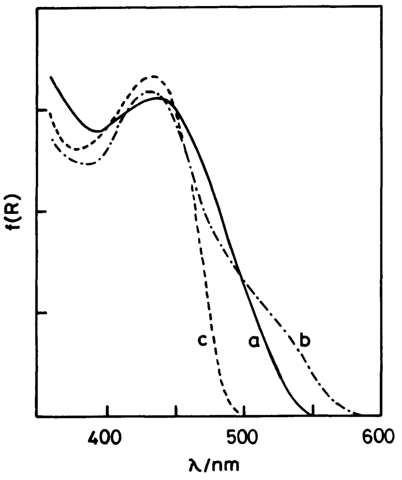

Fig. 3. Diffuse reflection spectra of (a) the orange-colored pyrene-N-butyl-2,4,6-trinitroaniline complex, (b) red-colored pyrene-N-heptadecyl-2,4,6-trinitroaniline complex, and (c) the latter acceptor compound alone.

is formed first with the N-hexyl derivative. The melting point fluctuates around 60°C (see shaded circles) and then tends to raise slowly with marked alternation. If one assumes that the 1:1 composition found in Fig. 1d is applicable to all the complexes in the region III, the melting point under consideration may be congruent except for the cases of the N-hexyl, N-heptyl, and N-octyl derivatives. When the regions I and III are overlapped with each other, the orange and red complexes may be regarded as polymorphs. The primary factor in determining the mode of molecular packing would be the charge-transfer interaction in the former complexes and the compromise between the alkyl chain alignment and the charge-transfer interaction in the latter. As is indicated by the melting point alternation, with increase in the alkyl chain length the alignment becomes relatively more important. The region II, where the orange-colored 2:1 complexes are formed, occupies about two thirds of region III. It may be noted that N-alkyl-2,4,6-trinitroanilines themselves also exhibit the fall of the melting point with increase of the alkyl chain length in the lower homologues and rise in the higher homologues.

The visible spectra of the orange 1:1 complex and red 1:1 complex are shown in Fig. 3. The former is represented by the N-butyl-2,4,6-trinitroaniline complex and the latter by the N-heptadecyl-2,4,6-trinitroaniline complex. For the sake of comparison, the spectrum of the acceptor is also shown. The absorption in the range from 500 to 550 nm arising from the complex formation may account for the orange color. The additional absorption appearing in the red complex is weaker but extends to about 600 nm. A shoulder may be located at about 530 nm. The shift of the absorption band to the longer wavelength-side may be interpreted by the small resonance energies in the red complex, reflecting a mode of molecular packing unfavorable to the intermolecular charge-transfer interaction. Preliminary X-ray diffraction studies on the red complexes gave patterns with a strong peak in the proximity of $2\theta=3°$ in accordance with the parallel arrangement of the pentadecyl and heptadecyl chains.

In this connection, it may be worthwhile to mention the effects of alkyl chain length on complex formation in solution studied by Foster and Hammick.[5] They have determined the association constants for the interactions of N-alkylanilines with 1,3,5-trinitrobenzene and 2,4,6-trinitrotoluene in cyclohexane. According to their study, complexes of greater stability are formed with the higher homologues of both series; *e.g.*, the association constant is 8.2 $\mathrm{l\,mol^{-1}}$ for the N-butylaniline-1,3,5-trinitrobenzene complex and 11.6 $\mathrm{l\,mol^{-1}}$ for the corresponding N-dodecylaniline complex. The wavelength of the maximum absorption due to the charge-transfer interaction rises with the first few homologues of both these series, thereafter remaining sensibly constant. Because of the three dimensional order, the effects of alkyl chain length on the stability of complexes in the solid state are entirely different from those observed for the complexes in solution.

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