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NOTE

Selective Solubilization of Polynuclear Aromatics (PNA's) in Aqueous Media

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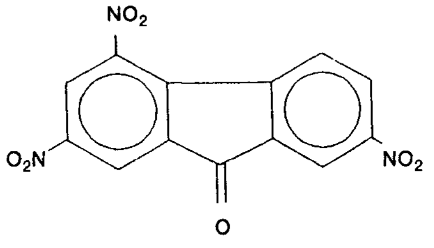
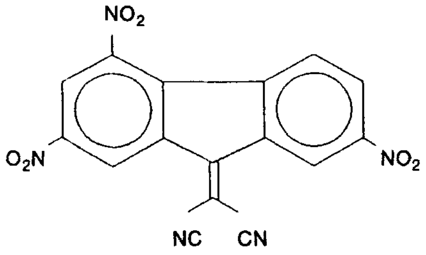
INTRODUCTION

The use of 2,4,7-trinitrofluoren-9-one (TNF) or a TNF derivative, 9-dicyanomethylene-2,4,7-trinitrofluorene (DTF), as an agent for complexing various aromatics has been well documented (*1–4*).



TNF



DTF

The electron-deficient TNF or DTF interacts with several aromatic donor types, including PNA hydrocarbons, hetero-atom containing PNA's, and anilines. The species formed, known as electron donor-acceptor complexes, are characteristically more highly colored than either component,

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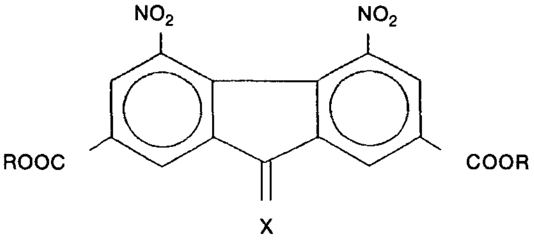
and are typically generated in organic solvents such as chloroform and dichloromethane. Several TNF derivatives such as simple esters and amides have been used as solid-state acceptors in electrophotographic processes (*5*, *6*). We recognized a potential application for related water-soluble TNF derivatives that could selectively solubilize PNA's in an aqueous phase. Such materials could find use as extractants for the removal of PNA's and related species from lubricating oils and other petroleum fractions. Although removed to some extent by conventional refining processes, the residual PNA content of petroleum products is of current concern to petroleum processors because of the carcinogenic nature of many PNA's. It is our belief that more selective and efficient extraction systems may be developed using polynitrofluorenones.

RESULTS AND DISCUSSION

Derivatives of 4,5-dinitrofluoren-9-one-2,7-dicarboxylic acid **1** (*7*, *8*) have proven promising as complexing extractants. Both the polyethylene glycol monomethyl ether (PEGME; MW 750) diester **2** and its dicyanomethylene analog **3** have been examined. It is noteworthy that both **2** and **3** are more highly colored than one might expect—**2** is a rich orange while **3** is a dark green. We suspect that the flexible polyether functionality is acting as an intramolecular electron donor, and that this interaction results in absorption at longer wavelengths than is seen in the simple esters (*8*).



1 $R = H, X = O$

2 $R = (CH_2CH_2O)_{\bar{n}}CH_3$ $(\bar{n} = 16.3)$, $X = O$

3 $R = (CH_2CH_2O)_{\bar{n}}CH_3$ $(\bar{n} = 16.3)$, $X = C(CN)_2$

Competitive extractions were carried out to determine the relative extractability of several PNA's. A heptane solution containing 0.01 *M* of each PNA and 0.005 *M* hexadecane as internal standard was shaken with an equal volume of an aqueous solution (pH ≈ 3) containing 5 wt% (~0.03 *M*) of **2** or **3**. In such experiments the solution of **2** became more red-orange, and the solution of **3** changed from green to orange. Gas chromatography was used to follow the PNA concentrations in the heptane phase. The results of these extractions are shown in Table 1. It is

TABLE 1
Mole Fractions of PNA's Extracted by Diesters **2** and **3**

PNA	**3**	**2**
Naphthalene	0.007	0.001
Dibenzothiophene	0.120	0.106
Phenanthrene	0.200	0.109
Pyrene	0.514[a]	0.100[a]

[a] Determined in separate experiment vs phenanthrene and normalized.

apparent that the extractability of the PNA's by **3** parallels the increase in number of fused rings in the PNA. With the weaker electron acceptor **2**, however, the lack of distinction between the latter three PNA's is rationalized as a moderating of aqueous complex formation by the increasing size of the hydrophobic PNA moiety.

The effects of pH and temperature were studied because of their possible relevance to selectivity and extractant regeneration. The pH of the aqueous phase has little effect on the extraction of phenanthrene when **2** is used in the pH range of 3–8 (citric acid–disodium hydrogen phosphate buffer system). Similar experiments with **3** showed a falling off of complexation with increasing pH. However, this change was irreversible and associated with a marked color change, from green to black-purple, over the pH range. The nature of the change is not understood. The effect of increasing temperature is to reduce the amount of a PNA that is solubilized in the aqueous phase. The results for **2** and **3** with phenanthrene and pyrene are shown in Fig. 1. From a practical point of view, temperature cycling might be used to facilitate the regeneration of acceptor solutions.

A multistage extraction of phenanthrene from heptane using a 5 wt% aqueous solution of **3** was carried out at 25°C to test the regenerative ability of such systems. The aqueous solution was alternately equilibrated with 0.10 *M* phenanthrene in heptane and with pure heptane. After several cycles the amount of phenanthrene in each heptane strip phase was determined. After an initial partial loss of activity, the ability of the solution of **3** to extract phenanthrene stabilized at 77% of the original value. Also, the amount of phenanthrene recovered in each cycle suggested that approximately 25% of the molecules of **3** were associated with phenanthrene molecules before stripping.

Other experiments showed that the structure of the complexing agent must be carefully chosen to ensure proper performance. Thus, PEGME and polyol esters of 2,5,7-trinitrofluoren-9-one-4-carboxylic acid (carboxy derivative of TNF) (*7, 9*) were highly water-soluble and readily complexed

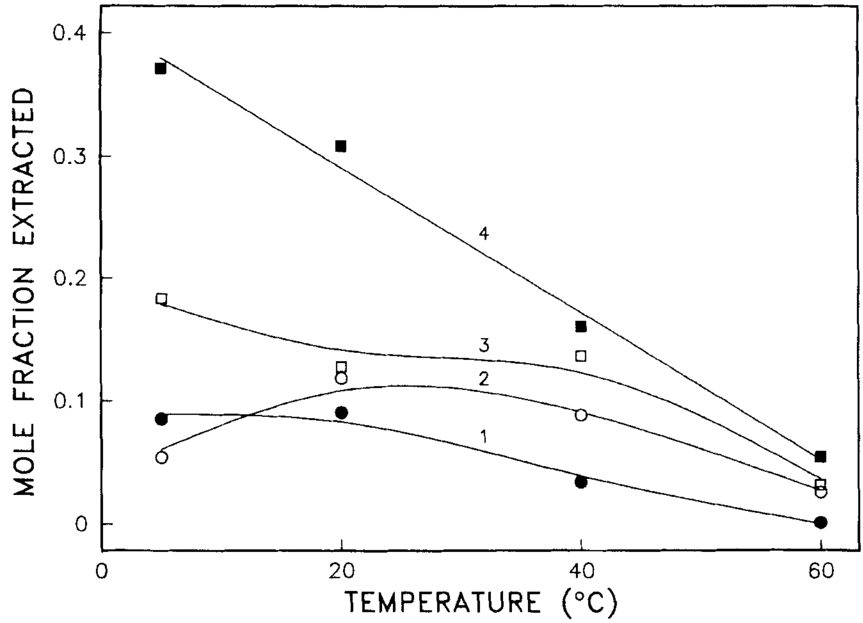


FIG. 1. Temperature dependence of extraction of phenanthrene and pyrene from heptane. (1) Pyrene extracted by **2**. (2) Phenanthrene extracted by **2**. (3) Phenanthrene extracted by **3**. (4) Pyrene extracted by **3**.

with PNA's, but the complexes tended to form emulsions or were incompletely soluble in the aqueous phase.

The above results suggest that water-soluble fluorenone derivatives, including the esters discussed here, may prove to be viable extractants for PNA's. Experiments with higher PNA's and with actual refinery streams will further define the applicability of these extractants.

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