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DSC STUDY OF CHARGE-TRANSFER COMPLEXES OF POLYNUCLEAR AROMATIC HYDROCARBONS WITH NITROAROMATIC ACCEPTORS

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ABSTRACT

Charge-transfer, crystalline complexes of 1,3,5-trinitrobenzene (TNB), 2,4,7-trinitro-9-fluorenone (TNF), and 2,4,5,7-tetranitro-9-fluorenone (TENF) with eleven polynuclear aromatic hydrocarbons were compared for thermal stability, ΔH and ΔS of melting. Factors possibly influencing the above parameters are discussed.

Melting does not induce separation of the components; these complexes can be repeatedly crystallized and melted without variation of the ΔH of melting, thereby indicating high thermal stability.

With a few exceptions, melting temperatures of the complexes increase in the order TNB<TNF<TENF: so do ΔH and ΔS of melting. A number of crystal transitions were observed.

INTRODUCTION

The factors which determine the thermal stability of crystalline charge-transfer complexes have been qualitatively known for some time[1]. However, the expression in quantitative terms of the corrrelations of the above factors with thermal stability has met substantial difficulties. More than the electronic interactions between the partner molecules in the complex, reticular forces in the complex crystal play a major role in establishing the thermal behavior of the complex.

Reticular forces should evidently be controlled by molecular factors of the moieties in the complex, such as the relative size and shape of the donor and the acceptor.

In our previous papers[2–5] on complexing of polynuclear aromatic hydrocarbons (PAH) with two electron acceptors, namely pyromellitic dianhydride (PMDA) and mellitic trianhydride (MTA) we evidenced that the crystalline complexes obtained undergo decomposition or melting at temperatures higher than the melting temperature of the free hydrocarbon. A satisfactory comparison by DSC of the two series of complexes with the two acceptors could not be established, because the TMA complexes decompose on heating without prior melting. This is probably due to the carbonization of the acceptor molecule starting around 300°C.

To verify possible correlations of thermal behavior as determined by DSC and the parameters of thermal stability of crystal complexes of this kind, we prepared and examined a series of complexes of PAHs with acceptors structurally related. We considered as electron acceptor the polynitroaromatic compounds s.trinitrobenzene, 2,4,7-trinitrofluorenone, and 2,4,5,7-tetranitrofluorenone.

The complexes of the PAHs considered for our work, with s.trinitrobenzene[6] and with trinitrofluorenone[6,7] are largely known. Only three complexes of PAHs with tetranitrofluorenone are recorded in the literature[8].

EXPERIMENTAL

Reagents and apparatus

1,3,5-Trinitrobenzene (TNB) Eastman Kodak Co., Rochester, N.Y.; 2,4,7-trinitro-9-fluorenone (TNF) and 2,4,5,7-tetranitro-9-fluorenone (TENF) Aldrich Chemical Co.

All the PAHs were from Fluka AG, Buchs, Switzerland.

Differential scanning calorimeter, Perkin-Elmer, DSC model 1B.

Preparation of the complexes

The complexes with TNB were prepared by crystallization from methanol, ethanol, or chloroform; those with TNF by crystallization from methylethylketone and recrystallized from benzene; those with TENF by crystallization from methylethylketone.

All the complexes were analyzed by IR and UV spectroscopy. Donor–acceptor ratio (stoichiometry) was found 1:1 in all the cases examined here.

DSC runs

From 2 to 4 mg of sample, sealed in aluminum pans for volatile samples, were heated under nitrogen flow, from 30°C to complete melting of the sample.

Heating rate 16°C min^{-1}; instrument sensitivity 8 mcal sec^{-1}. The melt obtained was cooled, kept at room temperature during one hour, then re-heated in the calorimeter.

For each sample at least three heating–cooling cycles were run.

Instrument calibration was by a standard indium sample (99.999% purity) of known temperature (156°C) and enthalpy (−6.79 kcal g^{-1}) of melting.

Transition and melting temperatures, and areas of the peaks were reported as in our previous work[6]. In conformity with our former work, we reported in tables the data from the second melting of the complexes.

IR spectra of all the complexes were recorded (Nujol) of the material crystallized from solvent and of the same material solidified after melting.

When the IR spectra of the complex solidified from the melt did not superimpose to that of the complex crystallized from a solvent, X-ray diffraction patterns were obtained. X-ray patterns were also run on complexes showing a peak before melting.

RESULTS

Figure 1 shows typical thermograms of this class of complexes.

Table 1 reports thermodynamic data (T_f, ΔH, ΔS) for the acceptors in their normal crystalline form. The corresponding data for the hydrocarbons were reported in a previous paper[9].

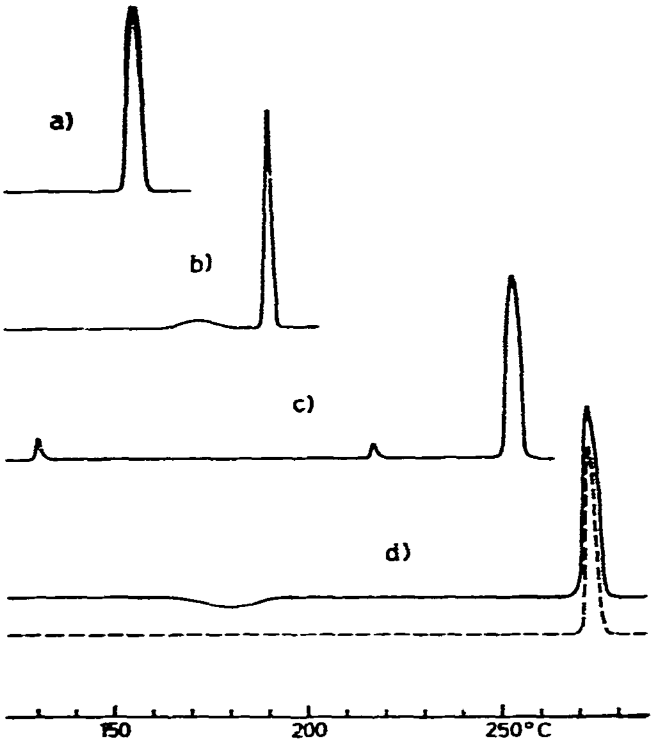

Fig. 1. Examples of DSC thermograms of complexes formed by PAHs with polynitroaromatic electron acceptors. (a) TNB–anthracene. "Regular" thermogram: the only peak shows the melting endotherm. (b) TNF–anthracene. Thermogram showing a crystal transition followed by melting. (c) TNB–pyrene. Thermogram showing two crystal transitions followed by melting. (d) TNF–perylene. Thermograms of first melting (full line) and of re-melting (dashed line). During first melting a crystal exothermic transition is shown before melting.

Table 2 reports T_f, ΔH, and ΔS data for the complexes formed by PAHs with TNB, TNF and TENF. The standard deviations range from ±0.1 and ±0.6°C for T_f, from ±0.02 and ±0.4 kcal mol^{-1} for ΔH, and from ±0.1 and ±0.5 cal mol^{-1} K^{-1} for ΔS.

As mentioned in previous work[5], the shape of the melting peaks is affected by the granule size and by the degree of homogeneity of the samples. Samples run as

TABLE 1

THERMODYNAMIC DATA OF TNB, TNF AND TENF

Acceptor	$T_{trans.}$ (°*C*)	$\Delta H_{trans.}$ (*kcal* mol^{-1})	$T_{fus.}$ (°*C*)	$\Delta H_{fus.}$ (*kcal* mol^{-1})	$\Delta S_{fus.}$ (*cal* mol^{-1} K^{-1}).
TNB			12.1 ± 0.2	5.4 ± 0.2	13.9 ± 0.5
TNF	157	1 ± 0.04	177 ± 0.4	5.5 ± 0.2	12.2 ± 0.3
TENF			255.2 ± 0.3	7.5 ± 0.2	14.1 ± 0.3

obtained by crystallization from solvents thus gave non-reproducible thermograms. Values given in the tables refer to measurements performed after the samples had melted and had been allowed to recrystallize in the DSC pans; the T_f values measured on the second and successive melting were reproducible. The same applies for the ΔH values, except a few cases discussed below; (the ΔH measured on second and successive melting was generally the same as those obtained from the rather distorted peaks observed on first melting, except in those cases in which crystalline transitions occur after the melting temperature).

ΔH and ΔS values were obtained from the peak of first melting only for the 1,12-benzoperylene–TNB complex. This complex actually dissociates slowly on heating, as shown by the appearance, on thermograms re-run after the first melting–cooling cycle, of a peak melting temperature of the "free" hydrocarbons. The intensity of this peak increases on going from the second to successive runs, with corresponding decrease of the melting peak of the complex. The dissociation of the complex after a few heating–cooling cycles is evident from the IR spectra of the 1,2-benzoperylene complexes with a previous thermal history, which show bands of the complexed and of the uncomplexed hydrocarbon.

As shown in the examples of Fig. 1, a few complexes show one peak (two in the case of pyrene–TNB) attributable to crystal transitions occurring before melting. It was observed in the present work that TENF itself exists in at least two different crystalline forms at room temperature. One form is obtained on crystallization from MEK, and the other on cooling the melt (complex). Both the IR spectrum and the X-ray powder diffraction of the latter form differ from those of the original one.

Though quite small, the ΔH involved in the crystalline transitions could be measured (Table 3), except for the perylene–TNB complex, whose peak is very broad. Whenever the crystalline transitions are irreversible, the change in the crystalline form was confirmed by the IR spectra and X-ray diffraction patterns.

Since the phenanthrene–TNB complex shows, before melting, an irreversible peak of unusual intensity as compared to the peak normally observed for crystalline transitions, the X-ray diffraction pattern of this complex was taken at different temperatures. It was thus confirmed that the above peak is associated with a high energy crystalline transition.

TABLE 2

THERMODYNAMIC DATA ON D-A COMPLEXES OF POLYNITRO-AROMATIC COMPOUNDS WITH PAHs

Hydrocarbon	*TNB*			*TNF*			*TENF*		
	m.p. (°C)	ΔH_f (*kcal mol*$^{-1}$)	ΔS_f (*cal mol*$^{-1}$ °C^{-1})	*m.p.* (°C)	ΔH_f (*kcal mol*$^{-1}$)	ΔS_f (*cal mol*$^{-1}$ °C^{-1})	*m.p.* (°C)	ΔH_f (*kcal mol*$^{-1}$)	ΔS_f (*cal mol*$^{-1}$ °C^{-1})
Anthracene	165.5	9.5	21.6	193.3	10.8	23.2	283.4	16.7	30.1
Phenanthrene[a]	164.6	6.5	14.9	195.5	9.8	20.9	237.8	11.8	23.1
3,4-Benzophenanthrene	153.4	10	23.5	170	10.5	23.7	233	13.1	25.8
Pyrene	253.3	9.2	17.5	246.4	10.5	20.2	240.3	10.6	20.5
Triphenylene	249.2	12.1	23.2	241	12.7	24.8	287.2	16.2	28.9
Chrysene[a]	189.1	10.5	22.9	250.7	13.9	26.5	280.8	15	27.1
1,2-Benzoanthracene	159.9	8.9	20.6	227.6	12.1	24	259.7	10.5	19.7
3,4-Benzopyrene	226.1	10.7	21.3	263.1	13.3	24.7	264.8	17	31.6
1,2,5,6-Dibenzoanthracene	235.7	14.5	28.5	273.8	12.6	23.1	288.5	14.1	25.2
Perylene	253.4	13.5	25.7	273.9	15.9	29.1	301.5	14.2	24.8
1,12-Benzoperylene	311.4	11.9[b]	20.3	294.3	9.8	17.4	282.2	12.8	23.1

[a] Measure on the first run. After melting-cooling the peak shrinks due to the slow decomposition of the complex. [b] These hydrocarbons show crystalline transitions in their normal crystalline form.

TABLE 3

CRYSTAL TRANSITIONS OF D–A COMPLEXES OF POLYNITRO-AROMATIC COMPOUNDS WITH PAHs

Hydrocarbon	*TNB*		*TNF*		*TENF*	
	m.p. (°*C*)	ΔH_t (*cal mol*$^{-1}$)	*m.p.* (°*C*)	ΔH_t (*cal mol*$^{-1}$)	*m.p.* (°*C*)	ΔH_t (*cal mol*$^{-1}$)
Anthracene			177	2624[a]		
Phenanthrene	148.2	2908[b]	172–182	n.m.		
Pyrene	129 215.5	563[b] 446[b]			217–220	2048[a]
Perylene	207–217	n.m.[a]	180	3109[d]		
1,12-Benzoperylene			197	1475[a]		
Chrysene					280.8[c]	
1,2-Benzoanthracene			227.6[c]			
1,2,5,6-Dibenzo-anthracene					288.2[c]	

[a] Non reversible transition. [b] Reversible transition. [c] Area of the first melting peak is higher than in the following runs; after melting the crystal form of the cooled solid is different. [d] Exothermic transition.

The IR spectra of the complexes 1,2-benzoanthracene–TNF and 1,2,5,6-dibenzoanthracene–TENF show slight differences when the samples are crystallized from MEK or from benzene. To throw light on this aspect, an X-ray investigation is under way.

Data on the complexes chrysene–TENF, 1,2-benzoanthracene–TNF and 1,2,5,6-dibenzoanthracene–TENF, which do not show any peaks before melting, were also inserted in Table 3. These complexes have a common feature, i.e., the area of the melting peak on first melting is larger than those recorded from successive runs.

IR spectra of the latter three complexes, crystallized from the melt, are slightly different from those of samples crystallized from a solvent. Slight differences are also noticeable in the X-ray diffraction patterns, possibly due to rearrangement of the crystal lattice.

The thermogram of the perylene–TNF complex is quite different from all the others. The complex can take two crystal forms: the first is obtained by crystallization from MEK or by melting–cooling–reheating up to 190°C; the second is obtained after each melting–cooling to room temperature. This behavior is illustrated in Fig. 1d. The complex, during the first heating, shows only the melting peak (dashed line); after melting, the solid assumes a different crystal form, which is stable only up to 150°C. Repeated DSC runs on the same sample show a hexothermic peak between 160 and 190°C, after which the sample reassumes the form of the complex crystallized from the solvent (full line).

DISCUSSION

The complexes studied are thermally stable, as they can undergo a number of heating–cooling cycles without decomposition, the only exception being the benzoperylene–TNB complex.

The ΔH of melting are very high as compared to those (Tab. 1 and ref. 9) of the respective acceptor and donor in their normal crystalline forms. The same was observed with the PAH–PMDA complexes[5].

Table 2 shows that—with a few exceptions—melting temperatures, ΔH and ΔS for the three series of complexes increase in the order TNB<TNF<TENF.

The color of the complexes becomes darker in the same order (e.g., the complex pyrene–TNB is orange, with TNF dark red, and with TENF black) apparently reflecting a corresponding shift of the charge-transfer bands toward low frequencies.

The values from the literature on TNB complexes[10] are actually lower than the corresponding values on TNF complexes[7].

As noticed from PAH–PMDA complexes[4], no relationships are apparent between the thermodynamic data and structural parameters, such as the ionization potential of the donor and ν_{CT} of the complex.

This was not unexpected, since the main contribution to the observed thermal phenomena is substantially due to the lattice energy of the crystalline complexes, the "coupling energy" (i.e., the energy involved in the formation of D–A pairs) being usually very low relative to the total energy.

Some support for the low contribution of complexing interactions to the observed enthalpies of fusion is obtained from values for enthalpies of picrate formation in the solid state—ca. 2–6 kcal mol^{-1} (ref. 11)— and from the data shown in Table 4. The values for enthalpies of complex formation are considerably less, in general, than the measured values of ΔH_f.

TABLE 4

VALUES (kcal mol^{-1}) FOR ($\Delta H_{f,DA} - \Delta H_{f,D} - \Delta H_{f,A}$) FOR HYDROCARBON COMPLEXES WITH POLYNITRO-AROMATIC ACCEPTORS[a]

Hydrocarbon	*TNB*	*TNF*	*TENF*
Anthracene	−2.79	+1.13	+2.31
Phenanthrene	−0.3	0.00	0.00
3,4-Benzophenanthrene	+0.7	+1.10	+1.7
Pyrene	+0.72	+0.91	+1.06
Triphenylene	+0.7	+1.20	+2.7
Chrysene	−1.92	+1.40	+0.48
1,2-Benzoanthracene	−0.29	+1.49	−2.11
3,4-Benzopyrene	−0.87	+1.63	+3.33
1,2,5,6-Dibenzoanthracene	+1.65	−0.35	−0.85
Perylene	+0.51	+5.92	−0.89
1,12-Benzoperylene	+2.35	+1.62	+1.15

[a] These values include any transition enthalpies from Table 3.

If it is assumed that only little dissociation of the complex occurs upon melting and that there is no loss of material by evaporation, sublimation, etc., then the experimental heats of fusion are easily related in the cycle.

$$\begin{tikzcd}
\text{solid} & D_s \arrow[d, "\Delta H_{f,D}"] & + & A_s \arrow[d, "\Delta H_{f,A}"] \arrow[r, shift left, harpoon, "\Delta H^\circ_s"] & D.A_s \arrow[l, shift left, harpoon] \arrow[d, "\Delta H_{f,DA}"] \\
\text{liquid} & D_l & + & A_l \arrow[r, shift left, harpoon, "\Delta H^\circ_l"] & D.A_l \arrow[l, shift left, harpoon]
\end{tikzcd}$$

where ΔH°_s and ΔH°_l are the heats of formation of solid and liquid complexes from solid and liquid components, respectively. Hence

$$\Delta H_{f,DA}-\Delta H_{f,D}-\Delta H_{f,A} = \Delta H^\circ_l-\Delta H^\circ_s$$

and values of $(\Delta H_{f,DA}-\Delta H_{f,D}-\Delta H_{f,A})$ are shown in Table 4. Values for the heats of mixing of liquid components and complex may be assumed to be very close to zero for solvents which do not interact with the compounds[11], and thus ΔH°_l may be approximated by values for complex formation in solution. For many charge-transfer complexes in solution enthalpies of complex formation are ca. 2 kcal mol^{-1} and these are less than enthalpies of complex formation in the solid state[6].

Numerous workers have shown that enthalpies of complex formation increase as the free energies increase, i.e., that the stronger the interaction the larger the $-\Delta H^\circ$ value[6]. Thus, for a given donor with several acceptors, the larger the value of $(\Delta H_{f,DA}-\Delta H_{f,D}-\Delta H_{f,A})$ the stronger the complex formed.

In accord with the decreasing charge-transfer transition energies on substituting TENF or TNF for TNB as acceptor, the values of Table 4 show that increasingly greater interaction occurs in the same order for most donor hydrocarbons. For 1,2,5,6-dibenzoanthracene and 1,12-benzoperylene the reverse is true, however, suggesting the possibility of unfavourable steric interactions or disordered crystals, causing significant dissociation on melting (see Discussion re 1,12-benzoperylene–TNB complex). Some other irregularities can be noted from Table 4, but the data are in broad agreement with an increase in complexing interaction with the electron affinity of the acceptor molecule. If a value of ca. -2 kcal mol^{-1} is assumed for ΔH°_l, then values of ΔH°_s in the range -1 to -5 kcal mol^{-1} are derived in accord with expectation.

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