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THERMOCHEMICAL STUDY OF 2,6-DINITROTOLUENE

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ABSTRACT

The enthalpy of transition between two crystal forms of 2,6-dinitrotoluene was determined and the heat capacities of the respective forms in the solid and liquid phase were measured. The standard enthalpies of combustion, and the standard enthalpies of formation for the two forms were also determined.

INTRODUCTION

This is a systematic investigation of a nitroaromatic compound that is of interest to the explosives industry [1]. The existence of several isomeric forms of the dinitrotoluenes has long been established [2], and some single-crystal X-ray data have been more recently established [3]. A preliminary differential scanning calorimetric (DSC) experiment carried out in this laboratory confirmed that there are at least two major crystal modifications of the pure compound.

EXPERIMENTAL

Materials and synthesis

2,6-Dinitrotoluene

A commercially obtained sample (BDH) was recrystallised five times from sodium-dried benzene (BDH, AnalaR grade), dried in air, and stored in a vacuum desiccator over silica gel in the dark. Microanalysis of the purified compound gave satisfactory results, see Table 1. A purity de-

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TABLE 1

Microanalysis of purified 2,6-dinitrotoluene (M.W. 182.138), $C_7H_6N_2O_4(s)$

	Expected (%)	Found (%)
Carbon	46.16	46.33
Hydrogen	3.32	3.30
Nitrogen	15.38	15.47

termination using a DSC (Perkin–Elmer, model 2) indicated a purity of 99.93%; indium metal (purity 99.999%) was used as a calibrant. The compound melted sharply at 56.4 ° C; the literature value is 66 ° C [4]. A sample of the purified 2,6-DNT was placed in an oven (100 ° C) for 5 h, and after cooling under desiccation and subsequently scanning in the DSC, the literature value of 66 ° C was then found. In the following, [A] and [B] refer to the crystal modifications of lower and higher melting points respectively.

Differential scanning measurements

A hermetically sealed sample of 2,6-DNT[A] was scanned from 36.85 to 71.85 ° C. The resultant single-melt endotherm at 56.4 ° C is shown in Fig. 1(i). The sample was held at 71.85 ° C for about 10 min before being scanned down to 36.9 ° C, Fig. 1(ii). Two exotherms were then noted at 40.6 and 38.47 ° C respectively. The same sample was then scanned up to 71.85 ° C, Fig. 1(iii). The observed thermogram revealed three peaks at 51.1, 56.44 and 66.04 ° C respectively. The sample was once again cooled and then scanned up to 71.85 ° C, Fig. 1(iv). This time the thermogram revealed two peaks only, at 51.1 and 66.04 ° C. This cooling and heating process was then repeated several times. Each scan revealed only two peaks, but the first endotherm at 51.1 ° C was each time significantly reduced in size. The final scan, Fig. 1(v), produced a single peak of similar shape to that obtained from a sample of [B]. From these results, enthalpies of fusion were calculated: $\Delta_{\text{fus}}H^{\ominus}[\text{A}] = 19.28$ kJ mol^{-1}, and $\Delta_{\text{fus}}H^{\ominus}[\text{B}] = 16.07$ kJ mol^{-1}.

Heat capacities

The heat capacities, $C_p^{\ominus}$, of both crystal forms ([A] and [B]) and their melts were measured on a pre-calibrated DSC2 using standard procedures, with the sample material hermetically sealed in the sample pan. To test that the instrument was functioning satisfactorily, the heat capacity of sodium chloride (BDH, AnalaR) was determined under identical conditions with satisfactory results [5]. All samples of 2,6-DNT were weighed before and after scanning to check the integrity of the seal and the experiments. All

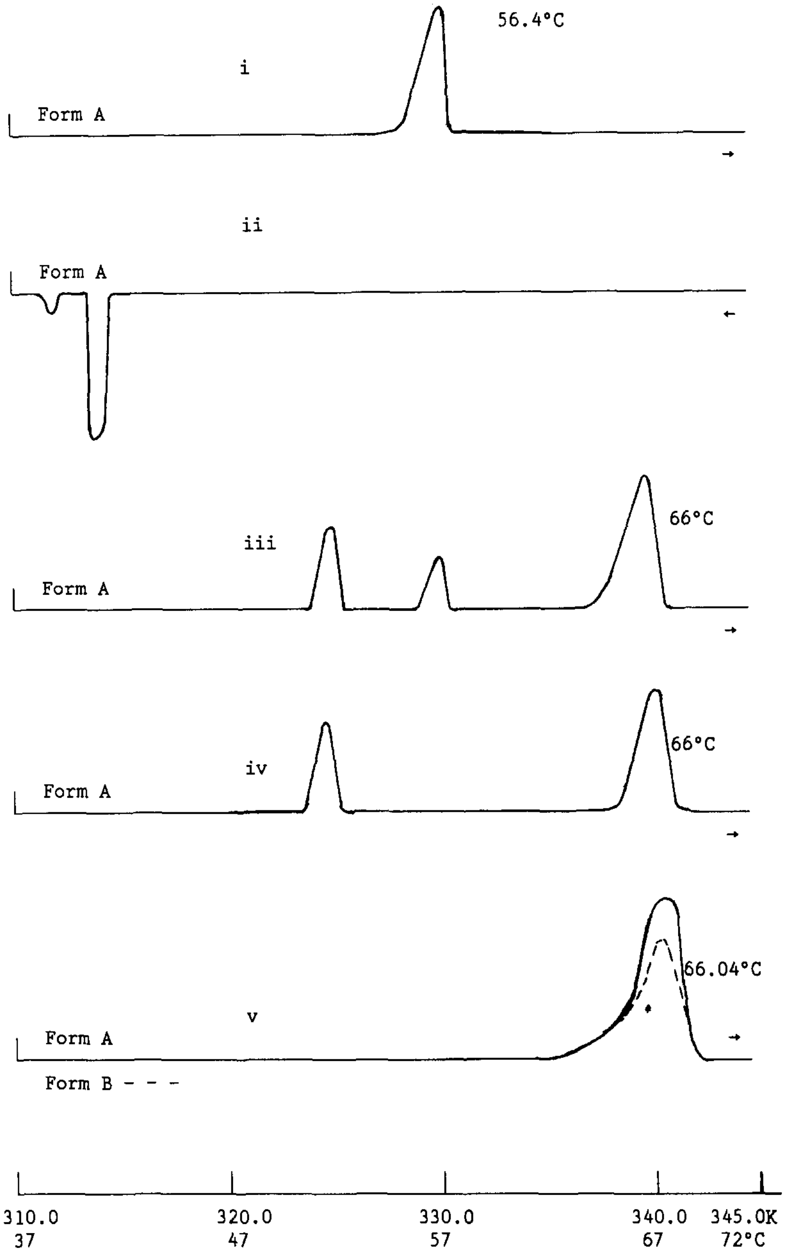

Fig. 1. Sequential study of the crystal transitions and fusion of 2,6-DNT.

measurements were performed in triplicate. The following masses were used:

Sample No.	1	2	3	4	5	6	7	8
Mass (mg)	5.09	4.97	6.66	3.53	5.51	4.77	5.21	7.78

The heat capacities obtained are tabulated in Tables 2–5. Plots of $C_p^\ominus$

TABLE 2

Heat capacity of 2,6-DNT solid [A]

T (K)	$C_p^{\ominus}$ (kJ mol^{-1} K^{-1})				Mean
	Sample 1	Sample 2	Sample 3	Sample 4	
305.0	0.216	0.218	0.216	0.217	0.217 ± 0.0015
307.5	0.222	0.221	0.221	0.221	0.221 ± 0.0007
310.0	0.223	0.224	0.223	0.223	0.223 ± 0.0004
312.5	0.231	0.231	0.231	0.231	0.231 ± 0.0003
315.0	0.232	0.229	0.224	0.229	0.228 ± 0.006
317.5	0.238	0.230	0.230	0.231	0.231 ± 0.001
320.0	0.238	0.230	0.240	0.235	0.236 ± 0.007

TABLE 3

Heat capacity of 2,6-DNT liquid [A]

T (K)	$C_p^{\ominus}$ (kJ mol^{-1} K^{-1})				Mean
	Sample 1	Sample 2	Sample 3	Sample 4	
335.0	0.260	0.261	0.255	0.260	0.259 ± 0.004
337.5	0.261	0.261	0.264	0.261	0.262 ± 0.002
340.0	0.278	0.268	0.264	0.270	0.270 ± 0.009
342.5	0.265	0.269	0.265	0.267	0.266 ± 0.003
345.0	0.270	0.271	0.268	0.270	0.270 ± 0.002
347.5	0.273	0.271	0.272	0.272	0.272 ± 0.001
350.0	0.276	0.275	0.274	0.275	0.275 ± 0.001
352.5	0.276	0.276	0.279	0.277	0.277 ± 0.002
355.0	0.278	0.277	0.283	0.278	0.279 ± 0.004
357.5	0.274	0.278	0.282	0.278	0.278 ± 0.005
360.0	0.285	0.280	0.283	0.283	0.283 ± 0.003
362.5	0.281	0.281	0.283	0.284	0.282 ± 0.003
365.0	0.282	0.282	0.284	0.282	0.283 ± 0.002

TABLE 4

Heat capacity of 2,6-DNT solid [B]

T (K)	$C_p^{\ominus}$ (kJ mol^{-1} K^{-1})				Mean
	Sample 5	Sample 6	Sample 7	Sample 8	
305.0	0.223	0.224	0.224	0.224	0.224 ± 0.001
307.5	0.225	0.226	0.225	0.225	0.225 ± 0.001
310.0	0.229	0.225	0.226	0.227	0.227 ± 0.002
312.5	0.224	0.227	0.227	0.229	0.227 ± 0.0035
315.0	0.231	0.237	0.230	0.231	0.232 ± 0.005
317.5	0.236	0.236	0.232	0.235	0.235 ± 0.0025
320.0	0.233	0.235	0.247	0.240	0.237 ± 0.006
322.5	0.241	0.240	0.246	0.249	0.244 ± 0.006
325.0	0.240	0.244	0.250	0.250	0.246 ± 0.007
327.5	0.251	0.252	0.258	0.251	0.253 ± 0.0065
330.0	0.268	0.268	0.267	0.265	0.267 ± 0.002

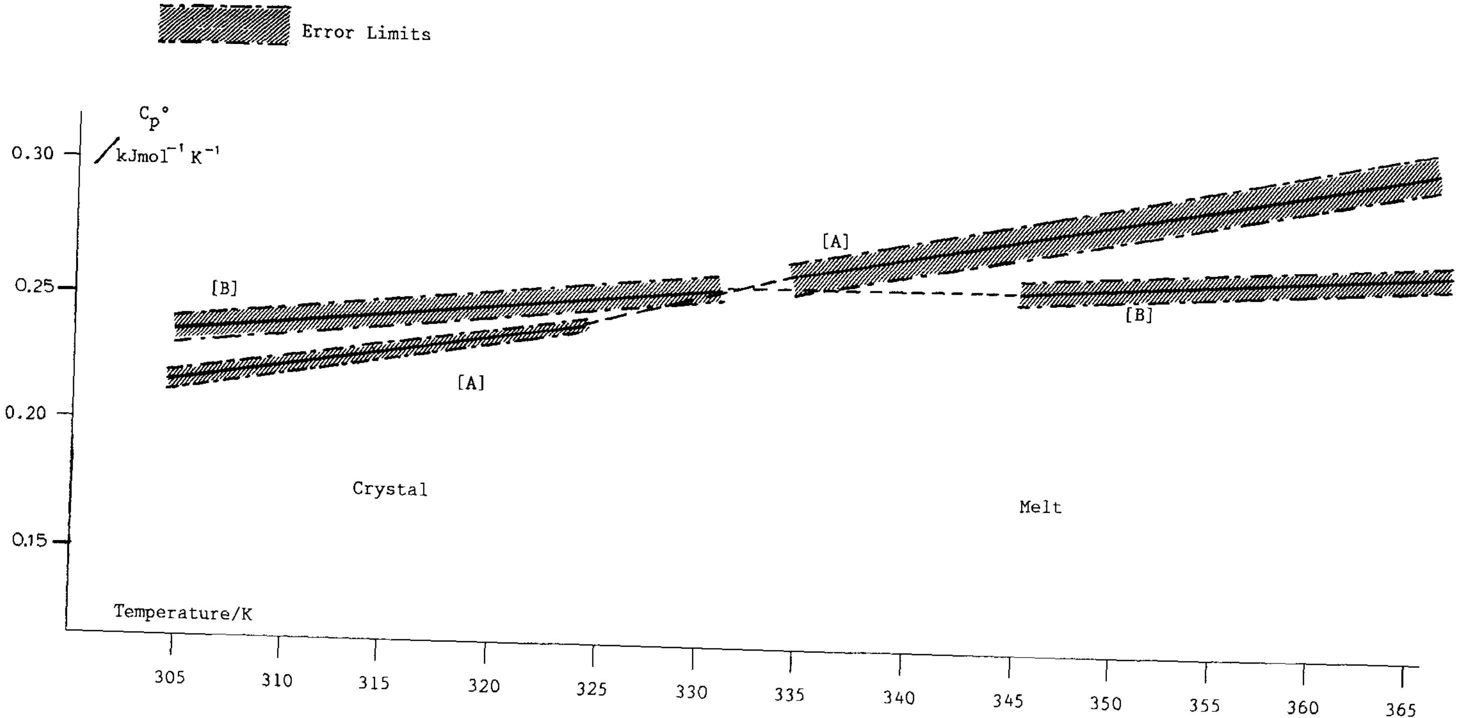

Fig. 2. Heat capacity $C_p^\ominus$ as a function of temperature for 2,6-dinitrotoluene ([A] and [B]), and the melts.

TABLE 5

Heat capacity of 2,6-DNT liquid [B]

T (K)	$C_p^{\ominus}$ (kJ mol^{-1} K^{-1})				Mean
	Sample 5	Sample 6	Sample 7	Sample 8	
345.0	0.260	0.261	0.257	0.260	0.260 ± 0.002
347.5	0.261	0.262	0.258	0.261	0.261 ± 0.002
350.0	0.262	0.262	0.254	0.262	0.263 ± 0.002
352.5	0.264	0.262	0.265	0.263	0.263 ± 0.002
355.0	0.265	0.269	0.265	0.263	0.265 ± 0.004
357.5	0.266	0.265	0.267	0.264	0.265 ± 0.002
360.0	0.266	0.265	0.268	0.264	0.266 ± 0.0025
362.5	0.268	0.264	0.268	0.266	0.267 ± 0.003
365.0	0.269	0.270	0.269	0.268	0.270 ± 0.001

against temperature are shown in Fig. 2; confidence limits are indicated by the broken lines. The results of a statistical analysis of the data are shown in Table 6.

Combustion calorimetry

The enthalpy of formation, $\Delta_f H^{\ominus}$, was determined for each form, see Table 7: runs 1–6 refer to [A], and runs 7–12 refer to [B]. Equation (1) was used to calculate $\Delta_f H^{\ominus}$ from the standard energies of combustion, $\Delta_c U^{\ominus}$, and the standard enthalpies of combustion, $\Delta_c H^{\ominus}$. The results are displayed in Table 8.

$$C_7H_6N_2O_4(c) + \tfrac{13}{2}O_2(g) = 7CO_2(g) + 3H_2O(l) + N_2(g) \qquad (1)$$

Density measurements using a standard pycnometric method were made, giving the following values: [A], 1.51 and [B], 1.49 g cm^{-3}. These values were subsequently used for buoyancy correction purposes; values of 1.536 and 1.528 have been reported previously [3], but it is not certain whether a single modification was involved.

TABLE 6

Statistical analysis

	m	c	r
[A] (s)	0.00116	−0.135	0.953
[B] (s)	0.00078	0.0001	0.964
[A] (liq)	0.00154	−0.252	0.946
[B] (liq)	0.00043	0.112	0.977

Values of heat capacities, $C_p^{\ominus}$, were fitted to the equation $C_p^{\ominus} = mT + c$ using standard statistical routines; T = temperature (K), r = correlation coefficient.

TABLE 7

Combustion calorimetry results for 2,6-dinitrotoluene

	1	2	3	4	5	6	7	8	9	10	11	12
M(sample) (g) [vacuo]	1.075269	0.9924756	0.9903342	0.9533105	1.002842	1.050023	1.013057	1.014838	1.136117	1.007264	1.02243	0.9404102
M(fuse) (g)	0.00486	0.00384	0.00468	0.00454	0.00458	0.00516	0.00428	0.00260	0.00476	0.00527	0.00450	0.0044
M(Pt wire) (g)	0.00781	0.00908	0.00777	0.00776	0.00668	0.008859	0.0078	0.00652	0.00574	0.00781	0.00702	0.00824
M(silica crucible) (g)	7.31934	2.79518	3.42786	2.79520	3.42792	3.42794	7.31920	3.42786	3.42782	7.31912	3.42784	7.3191
M(soot) (g)	0.00084	0.00060	0.00120	0.00044	0.0005	0.00060	0.00040	0.00050	0.00036	0.0006	0.00879	0.00080
$M(H_2O)$ (l)	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8	10.8
q_i (kJ)	0.8683139	0.0689916	0.0836832	0.0812346	0.08193419	0.09207839	0.0766872	0.047304	0.08508239	0.9400229	0.080535	0.0794856
q_n (kJ)	0.0734556	0.0668864	0.062706	0.0609144	0.0677822	0.0722612	0.0680808	0.0677822	0.07465	0.0674836	0.0680808	0.05972
q_c (kJ)	0.02772	0.0198	0.0396	0.01452	0.0165	0.0198	0.0132	0.0165	0.01188	0.0198	0.029007	0.0264
q_w (kJ)	0.0319343	0.0293722	0.0293547	0.0282013	0.02969109	0.03114128	0.03000968	0.0300700	0.0387079	0.02983306	0.03030299	0.02780495
$\Delta\theta$(K)	2.4407	2.2547	2.2503	2.1626	2.2795	2.3873	2.2970	2.300	2.5803	2.2887	2.3155	2.1342
E_{cf} (kJ K^{-1})	0.0619706	0.0583905	0.0588675	0.0583232	0.05888884	0.05897004	0.06186388	0.05890934	0.05911714	0.06185388	0.0589221	0.06173931
$-\Delta U_c^\ominus$ (298.15 K) (kJ g^{-1})	19.57331	19.5885	19.60274	19.54296	19.588888	19.58448	19.54522	19.56235	19.57122	19.57612	19.52803	19.57264

TABLE 8

Energies of combustion and enthalpies of combustion of 2,6-DNT, [A] and [B] (kJ mol^{-1})

	[A]	[B]
$-\Delta_c U^\ominus$	3566.13 ± 3.82	3562.46 ± 3.64
$-\Delta_c H^\ominus$	3562.41 ± 3.82	3558.75 ± 3.64
$-\Delta_f H^\ominus$	49.65 ± 3.93	53.32 ± 3.75[a]

[a] Previous results are as follows: 53.12 [6], 50.21 [8] and 54.07 [4].

RESULTS AND CONCLUSIONS

It is clear that there are several crystal modifications of 2,6-DNT, of which at least two forms, [A] and [B], have thermodynamic stability. An estimate of the difference in stability may be derived from the present results, in terms of standard enthalpies of formation. From the combustion studies, directly, $\Delta_f H^\ominus[\mathrm{B}](\mathrm{s}) - \Delta_f H^\ominus[\mathrm{A}](\mathrm{s}) = 3.67$ kJ mol^{-1}. In view of the uncertainty limits quoted, this is not statistically significant, though it clearly establishes an order of magnitude. As shown in the following cycle, use of the DSC results depends on assumptions about the nature of the liquid product obtained from the melting processes.

$$\begin{tikzcd}
\text{2,6-DNT[A] (s)} \arrow[r, "\text{Fusion}"] \arrow[dr, dotted, "\text{Crystal transition}"'] & \text{Liquid melt} \\
 & \text{2,6-DNT[B] (s)} \arrow[u, "\text{Reversible fusion}"']
\end{tikzcd}$$

Since the heat capacity results indicate that the liquid states near the temperature region of fusion are *not* identical, the difference between the enthalpies of fusion, namely $19.28 - 16.09 = 3.21$ kJ mol^{-1}, does not directly give values for the difference between the enthalpies of formation. However, the value obtained is so very close to that derived from the combustion studies that we may be confident that any correction is small, with [B], as found, being the more stable. This is reasonable, as the heat content of the melts is unlikely to differ significantly.

An inherent difficulty in the study of crystalline solids of this nature is that of ensuring that a particular sample is wholly of one form. Powder X-ray studies in this Laboratory [7], while not conclusive, appear to show, from a comparison of the *d*-values of forms A and B with those calculated from the earlier X-ray investigation of Andreen and McCrone [3], that while forms A and B are clearly distinguishable, form [A] produced in this laboratory is not definitely identical in diffraction terms with that produced by Andreen and McCrone. A possibility exists that weak lines result from small quantities of form [B].

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