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Effect of extended electron delocalization on the thermal features of hexaamidocyclotriphosphazatriene. Differential thermal analysis

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Abstract

This paper discusses the thermodynamic shifts effected as a result of extending the electron cloud of a phosphazene ring over azo linkages to terminal hexa phenolic rings in a novel azo phosphorus compound. Hexaamidocyclotriphosphazatriene seems to exhibit a slightly puckered phosphazene ring with two sets of three amino groups; one below and the other above the molecular plane, which leads to a molecular structure belonging to the point symmetry group D_3. This could thermally be modified to the more symmetric point group D_{3h}. Because the difference between the two point groups is not really a massive structural change, the heat released upon the transfer at $T_c = 443$ K is relatively low. Reaction to the azo derivative, however, although it would not much modify the point group D_{3h}, could allow a larger change as a result of modified molecular resonance. This should mobilize the terminal phenolic protons sufficiently to stabilize the highly thermally stable azo $\rightleftharpoons$ hydrazo structure, which could effect a highly exothermic phase transition at higher $T_c = 603$ K. This discussion is based on the results of DTA which reveal shifts in ΔH, ΔS and activation energy at the phase transition as being greater by factors of respectively 5, 3–4 and only 2 for the azo derivative. The thermodynamic structural parameter α shows a minor structural shift of 0.02 in favour of the azo derivative; however, both structures still belong to the $3d$ Ising model.

INTRODUCTION

Hexachlorocyclotriphosphazatriene has attracted the interest of chemotherapists as it affords a successful synthesis of the important hexaamido derivative (hactp), which has found widespread applications as an anti-cancer drug and in chemistry and industry [1–4]. Despite the very interesting features of hactp [5], only a few publications have dealt with this compound, such as to report on its pyrolysis [3,6,7], electrolysis [8], hydrolysis [9] and a few thermodynamic [10] properties.

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The high molecular symmetry of the compound, which belongs to a slightly puckered D_3 point group (Scheme 1), together with a molecular structure built on a highly delocalized electron cloud at the phosphazene ring, has afforded a successful route to the synthesis [11] of an interesting azo derivative (Scheme 1), making use of the delocalization induced activation of the amino groups.

The aim of the present work has been to exploit the extremely high molecular resonance of the azo derivative to investigate induced shifts in specific heat, enthalpy and entropy changes, activation energy and other thermodynamic properties of hactp at the solid state phase transition, which could be interpreted in the light of varying molecular structure. The present thermal data have been discussed in terms of the influence of extended electron delocalization (which stretches from the core phosphazene ring over the azo linkages to terminal phenolic rings) throughout the molecular structure.

EXPERIMENTAL

Materials

Hactp was purchased from Nippon Soda Co. Ltd. (Japan) as a chemical compound incorporated in a massive excess of NH_4Cl. The results of DTA showed minor percentages of hactp revealed as exothermic transitions appearing at 443 and 513 K as shoulders on a major endothermic peak of NH_4Cl. Hactp was obtained as a pure substance after several cycles of CH_3OH/H_2O solvent extraction. The synthesis of the azo derivative [11] was performed following the established methods of diazotization and coupling with phenols [12]. The coupling with phenol was immediate. However, the resultant azo derivative required a few days to separate as a pure phase distinguished by a high light absorption and exhibiting dark brown crystals. The results of elemental analysis showed effective coupling to the hexaamino groups of the hactp compound. Although the azo derivative exists in the solid state, the compound is in equilibrium in the enantiomeric azo $\rightleftharpoons$ hydrazo structure [11], particularly at elevated temperatures. This is arguably a consequence of high electron delocalization induced mobility of the terminal phenolic protons.

Methods and equipment

The differential thermal analysis (DTA) of both hactp and its azo derivative was compared for samples weighing 0.03 g. The measurements were performed using a Shimadzu DSC TA 30 thermal analyser in the temperature range 300–700 K, with a temperature rise of 10 K min^{-1}. The thermal data were treated as previously described [13].

RESULTS AND DISCUSSION

The results of DTA of hactp hydrochloride (Fig. 1, left) have revealed a solid state structural phase transition at 443 K and melting at 513 K. These changes are associated with two exothermic peaks, the former being of relatively high intensity compared with the latter (which appears as a shoulder). The structure of hactp is expected to display a slightly puckered [14] planar phosphazene ring (Scheme 1), with two sets of three $^{+}NH_3$ Cl^- situated at the ring phosphorus atoms; one set is above and the other below the ring plane. This should lead to a molecular structure belonging to a reduced D_3 point group. The structural phase transition observed at 443 K could be associated with an allowed thermal rotation of the terminal amino groups into a less sterically hindered molecular structure of the higher point group D_{3h}, so that the minor difference in energy between the two

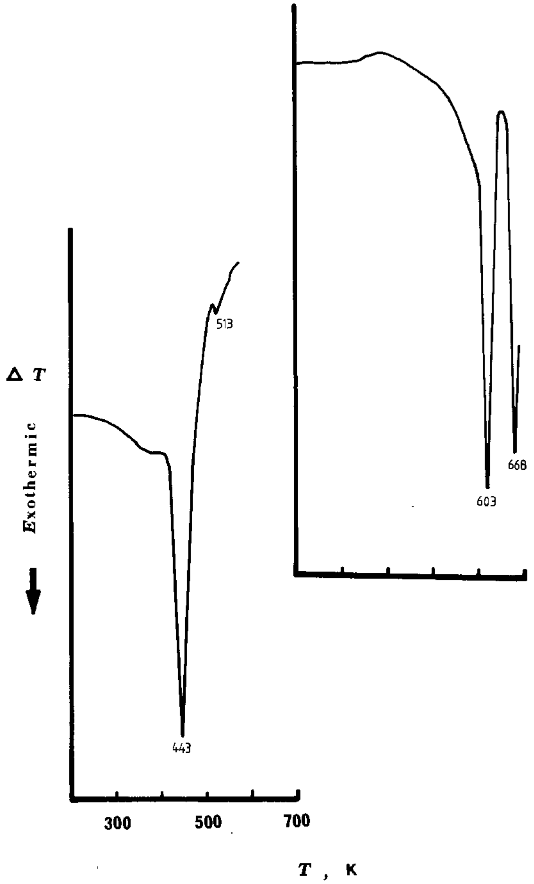
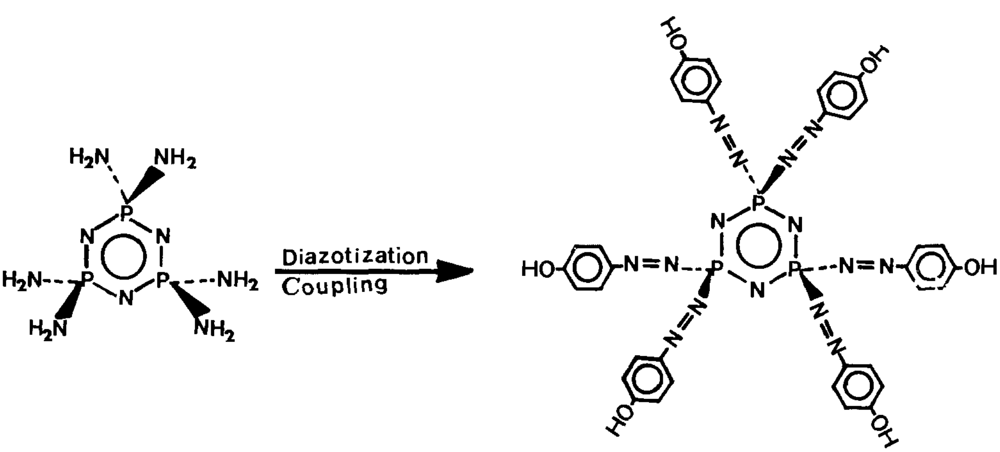


Fig. 1. Effect of extended electron delocalization on the T_c of hactp (left) and its azo derivative (right).



Scheme 1. Schematic representation of hactp reaction to form the azo derivative.

point groups could be released as a weak exothermic transition. The higher melting temperature, 513 K, with respect to the reported figure of 493 K [1–3] could be attributed to the presence of hactp in the hydrochloride form. The diazotization of this compound and eventual coupling with phenol to yield the azo derivative (Scheme 1) has shifted the T_c of both structural and melting phase transitions (Fig. 1, right) to 603 and 668 K respectively. The higher temperature shifts, 160 and 155 K respectively for the solid and melting phase transitions, should be a consequence of transfer into a more favoured structure with higher thermal stability; this could be a result of enhanced electron delocalization (Scheme 1) and, partly, of extensive intermolecular H-bonding in the resultant azo derivative.

Investigation of the specific heat of the solid state phase transition would clear up the results (Fig. 1) of DTA. A striking difference (Fig. 2) could confirm the proposed interpretation of the phase transition. Transfer of the molecular symmetry of hactp from D_3 into D_{3h} is not really a dramatic structural change, so that the resultant exothermic heat of the transition (Fig. 2, left) should be relatively low. In contrast, the solid state phase transition in the azo derivative is a matter of thermally enhanced proton mobility, which is assisted by the great electron delocalization, into the more favoured enantiomeric azo $\rightleftharpoons$ hydrazo structure of much higher thermal stability. Evidence of thermally enhanced proton mobility has recently been reported [11] for the azo derivative.

Calculation of the change in both ΔH and ΔS of the transition would further clarify the proposed interpretation. The azo derivative shows ΔH change of 181.52 J g^{-1}, which is almost five times the value of 35.19 J g^{-1} found for hactp. This would line up with the large difference (Fig. 2) in the specific heats observed for the two compounds. On the other hand, hactp shows a quite small ΔS change of 0.08 J g^{-1} K^{-1}, which is smaller by a

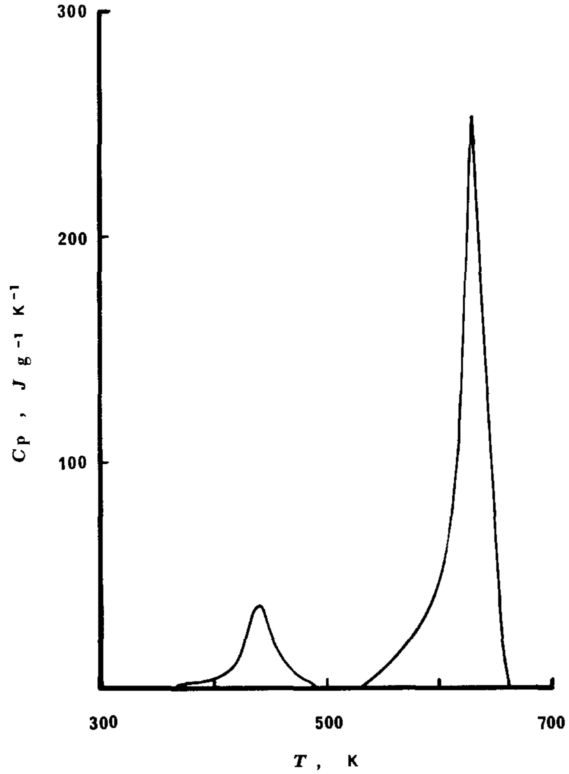


Fig. 2. A correlating illustration of the specific heat of hactp (left) and its azo derivative (right) at the solid state phase transition.

factor of 3–4 than the 0.29 J g^{-1} K^{-1} found for its azo derivative. The relatively low values of ΔH and ΔS changes of hactp correspond to the minor structural change, as proposed, from puckered D_3 into D_{3h}. The higher values for the azo derivative are associated with the structural shift into the highly thermal stable azo $\rightleftharpoons$ hydrazo structure.

Consistent with this discussion, the activation energy of the azo derivative shows a value (147.03 kJ g^{-1} K^{-1}) about twice that for hactp, 66.17 kJ g^{-1} K^{-1}. This correlation is estimated from the linear dependence shown in Fig. 3, and eqn. (1)

$$\ln \Delta C_p T^2 = \ln ZNU^2/R - U/RT \qquad (1)$$

where Z is the coordination number, N is the number of defects, R is the universal gas constant and U is the activation energy of the transition.

The smaller shift in the activation energy (by a factor of 2) compared with the higher difference in the enthalpy change (5-fold) would emphasize the fairly similar structural features displayed by the two compounds, with a high energy gap separating the enantiomeric forms of the azo derivative. This could be associated with thermally enhanced and high electron

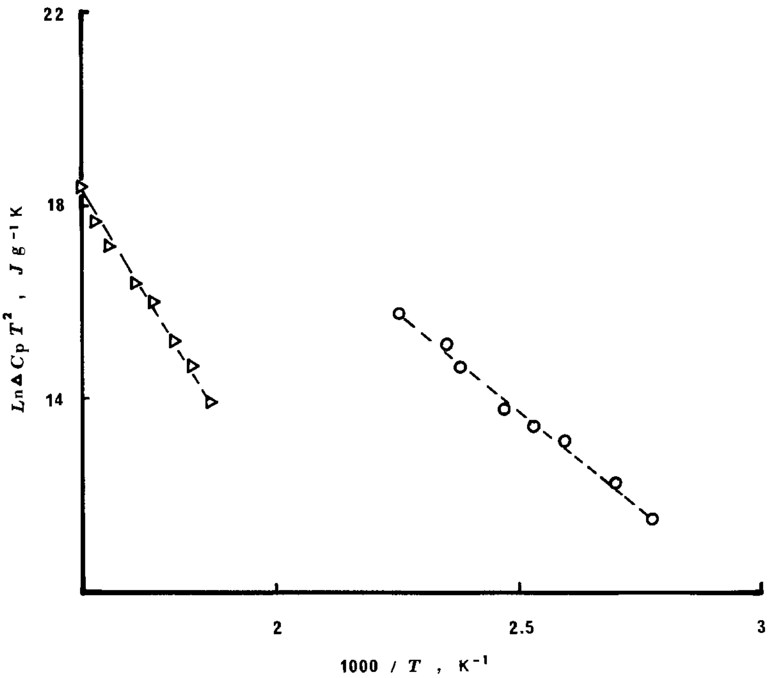


Fig. 3. Effect of extended electron delocalization on the linear dependence of the specific heat on the temperature for hactp (right) and its azo derivative (left).

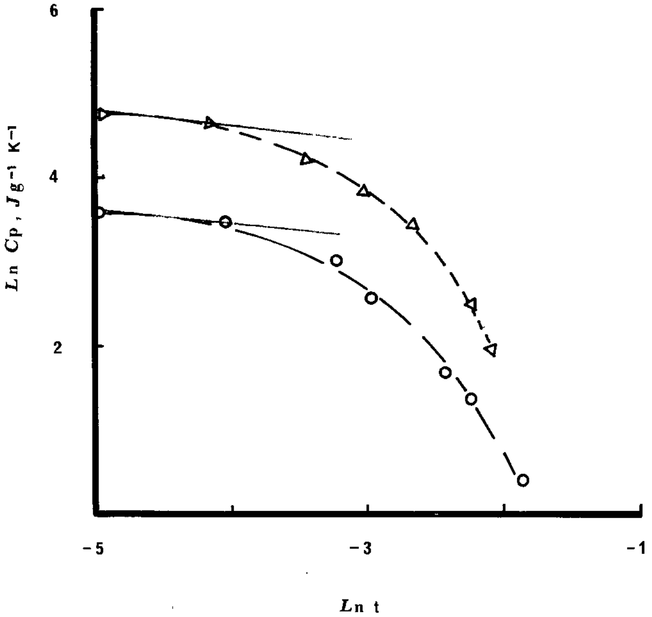


Fig. 4. Insignificant shift of the thermodynamic structural parameter α. Upper curve is for the azo derivative and lower one for hactp.

delocalization assisted proton mobility, shifting from the azo to the hydrazo structure.

In connection with the proposed minor structural change during the azo formation, identification of the model to which the phase transition could be referred has been essential. This could be determined using the thermodynamic structural parameter α from eqn. (2)

$$C_p = At^{-\alpha} \tag{2}$$

where A is a constant, $t = (T - T_c)/T_c$ and α is the thermodynamic structural parameter.

This parameter is appropriately calculated near the T_c (Fig. 4) of the transition. The calculated figures show a minor structural shift of 0.02 (0.15 − 0.13) in favour of the azo derivative, which would indicate almost similar structures belonging to the 3*d* Ising model [15,16].

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