Transformations in Thin Solid Layers: The Reversible Polymerization-Depolymerization of 2,6-Di-n-propyl-1,3,5,7-tetraoxa-2,6-dibora-4,8-octalindiones at Low Temperatures

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Dedicated to Professor Dr. Dr. h. c. mult. Günther Wilke on the occasion of his 60th birthday

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The course of Aggregation of molecules of the title compound (1b) through different, spectroscopically discernible and chemically identifiable forms of associations could be followed by matrix isolation and thin film infrared and UV-visible spectroscopy. It was found that molecules of 1b in thin films form clusters which at low temperatures interact weakly, probably through the carbonyl oxygens of one and the boron atoms of the neighbouring molecules. On warming to 260 K this association gradually takes the form of more defined chelate bonds, probably with ordered three-dimensional intermolecular structures. Above this temperature spontaneous formation of crystallites of the previously reported ‘hot’ and ‘cold’ modifications was observed. Studies with films of varying thickness indicate an interdependence of crystallite size and lattice energies.

Introduction

Aside from the numerous irreversible intra- and intermolecular reactions [1] there are only two fully reversible intermolecular solid state reactions to be found in the literature. In one [2], solid cyclopentadienyl-o-dithiobenzene)cobalt slowly and spontaneously dimerizes at room temperature and reverts to the monomeric form when heated to above 423 K. The other reaction of this type, recently described by one of us [3], is the solid state polymerization-depolymerization of the boron heterocycle 1 which occurs rapidly in both directions when the appropriate transition temperature is reached.

From the X-ray crystal analysis [3b], performed on the ‘hot’ and ‘cold’ modifications of 1a and 1c, it can be surmised that in their ‘hot’ form the molecules of all of the derivatives of 1 are arranged in a herringbone pattern in which the oxygen atoms of the two carbonyl groups of a molecule are both in close proximity of the boron atoms of the neighbouring parallel (1a, 3.1 Å) and near perpendicular (1a, 2.8 Å) molecules.

All derivatives of 1 [3a], with the exception of 1d (R= t-Bu), exhibited in their ‘hot’ form two infrared bands of near equal intensities at about 1770 and 1730 cm$^{-1}$. In the case of the t-butyl derivative, which showed only a single sharp carbonyl absorption band at 1775 cm$^{-1}$ it has been suggested that the
bulky substituent hinders a close approach of the molecules in the lattice, thereby preventing the lattice effects responsible for the observed double carbonyl bands in all of the other derivatives [3b]. Characteristically, these bands are replaced in the 'cold' form by two absorptions at about 1650 and 1550 cm$^{-1}$.

It thus appears that molecules of 1 can exist in three types of habitats depending on the substituents and temperature: The unassociated, the associated ('hot'), and the polymeric ('cold') forms. Intrigued by this rare case of lattice control of the chemical and spectroscopic environment of 1, we set out to further explore this solid state phenomenon by means of matrix isolation techniques.

**Results**

**Codeposition with argon at 12 K**

1b (yellow at room temperature and colourless at > 348 K) was codeposited with argon onto an optical window cooled to 12 K. The infrared spectrum (Fig. 2A) showed a very sharp carbonyl band (half-width 8 cm$^{-1}$) at 1791 cm$^{-1}$ as well as a multitude of lines centered around 1300 cm$^{-1}$ (1393 m, 1383 m, 1371 s, 1324 s, 1309 m, 1273 s, 1246 s), which are considerably sharper than those of the room temperature KBr spectra (Fig. 6a in ref. [4]). Furthermore, three weaker bands at 2970, 2940 and 2880 cm$^{-1}$ could be distinguished. The spectrum remained unchanged with time, under irradiation, and when annealed to 30 K.

The ultraviolet absorption spectrum (Fig. 2B) is marked by a band at 255 nm with shoulders at 261 and 272 nm. By comparison, a room temperature solid state ultraviolet spectrum of the same compound, suspended in paraffin sandwiched between silica plates, displayed a maximum at 280 nm with shoulders at about 270 and 295 nm.

**Film depositions at 12 K**

Results differ somewhat depending on whether they are obtained from thick films, suitable for infrared spectroscopic investigations, or from thin films, better suited for UV-Vis spectra. As more information could be gained from the infrared studies, the thick film results will be described first.

When 1b was sublimed onto the window at 12 K without a matrix, the infrared spectrum shown in Fig. 3A resulted: It shows a considerable broadening of all bands in the infrared spectrum and the shift of
the carbonyl band (half-width 45 cm$^{-1}$) to about 1768 cm$^{-1}$.

Allowing the temperature of the sample to rise slowly resulted in a gradual decrease of the carbonyl band concurrent with the development of a shoulder at lower wavenumbers, the growth of a strong band at 1272 cm$^{-1}$ and of a broad peak centered at 1600 cm$^{-1}$. Upon reaching about 100 K, the latter had given rise to a badly resolved triplet at 1635, 1575 and 1515 cm$^{-1}$. When the temperature was raised even further, this growth/decrease process continued until at about 260 K the spectrum shown in Fig. 3B was obtained.

Above 260 K three major changes could be observed simultaneously: The broadly structured band at about 1600 cm$^{-1}$ resolved into two peaks (a doublet at 1635/1610 and a band at 1546 cm$^{-1}$), in place of the absorption at 1768 cm$^{-1}$ two new bands of near equal intensities appeared at 1781 and 1745 cm$^{-1}$, and finally the 1272 cm$^{-1}$ absorption disappeared. Fig. 3C depicts the pattern after reaching a temperature of 300 K, a spectrum which is nearly identical to one described previously as that of the mixture of the ‘hot’ and ‘cold’ forms [4].

On cooling the chelated carbonyl bands grew at the expense of the ‘free’ carbonyl bands until, upon reaching 12 K, only a rest carbonyl absorption in form of a broad band at about 1760 cm$^{-1}$ remained as shown in Fig. 3D. The remainder of the spectrum below 1650 cm$^{-1}$ resembles strongly that of the ‘cold’, i.e., polymeric form which is normally obtained in KBr at room temperature (cf. Fig. 6b, ref. [4]). On reheating once again to 300 K a spectrum identical to that shown in Fig. 3C was obtained, and it was possible to cycle between these two extremes. In this process the spectra observed during the initial heating up run at the intermediate temperatures (Figs. 3A, 3B) did not recur.

Spectral shifts in the UV-Vis spectrum in general parallel this behaviour. The spectrum of films of 1b taken after sublimation at 12 K showed a single absorption band at 270 nm (Fig. 4A). Annealing the film to 260 K resulted in a gradual shift of this peak to 310 nm (Fig. 4B). Heating above 260 K gave rise to a spontaneous shift of this absorption to about 270 nm (Fig. 4C), while the infrared spectrum revealed only the presence of the carbonyl doublet at 1781 and 1745 cm$^{-1}$ (see insert Fig. 4C).

Upon recooling to 12 K the 270 nm absorption decreased and a new broad band grew in, centered at 390 nm (Fig. 4D), which resembles the solid state spectrum observed for the ‘cold’ form of 1b obtained.
Fig. 4. The UV-visible spectrum of 1b A) sublimed for 45 min as a film at 12 K, B) subsequently annealed to 240 K, C) warmed further to 300 K, and D) recooled to 12 K. The appropriate infrared spectra are inserted.

Fig. 5. The infrared absorption spectrum of 1b in the region 2000–600 cm\(^{-1}\) A) sublimed for 3.5 h as a film at 170 K, B) annealed to 300 K, and C) recooled to 12 K.
from a smeared suspension between silica plates [4]. The infrared spectrum showed a decrease of intensities of the 1781 and 1745 cm\(^{-1}\) bands and the rise of the absorptions at 1635 and 1546 cm\(^{-1}\) (see insert Fig. 4D).

Cycling of this film between the two extreme temperatures resulted in the recurrence of the respective spectra.

**Film deposition at 170 K**

The infrared spectrum of a film of 1b deposited at 170 K, a temperature chosen arbitrarily somewhere halfway between 12 K and 260 K, showed (Fig. 5A) the bands at 1767, 1638 and 1595 cm\(^{-1}\), indicating the presence of both associated and chelated carbonyl groups. Cooling this film to 12 K caused no changes in the infrared or UV-visible spectra. On warming this film to above 260 K the onset of a transformation could be observed. Reaching 300 K the bands at 1638 and 1595 cm\(^{-1}\) had vanished, a doublet, characteristic for the ‘hot’ modification, had grown in at 1780 and 1743 cm\(^{-1}\), as well as two weak bands at 1635 and 1545 cm\(^{-1}\) indicative for the presence of a trace of the ‘cold’ modification (Fig. 5B).

Cycling of this film between 300 K (Fig. 5B) and 12 K (Fig. 5C) resulted in the recurrence of the respective spectra.

**Discussion**

Molecules of 1b, when separated from each other in a matrix, possess a single sharp carbonyl band at 1791 cm\(^{-1}\). The high frequency of this carbonyl absorption, as compared to other ene-1,2-diesters, such as dimethylidioacetoxymuamate (\(\nu_{\text{max}} = 1742 \text{ cm}^{-1}\)) [6], is a reflection of the additional polarization of electron density towards the trivalent boron atoms in the isolated molecules of 1b.

In the absence of the matrix, the subliming molecules of 1b form a thin solid film on the cold surface of the window and assemble into aggregates, in which weak interactions, probably between the carbonyl oxygens of one and the boron atoms of the next molecule, give rise to varying degrees of intermolecular associations, similar to that found in fluids. This can be inferred from the shift of the carbonyl frequency to 1768 cm\(^{-1}\), from its broadening, and from the complementary observations of the long-wavelength shift of the UV absorption. In this habitat, the molecules are thought to be largely disordered and to represent a nearly amorphous state.

On warming from the near absolute zero temperature, the increased thermal mobility of the molecules allows a growing degree of self-organization concomitant with an increase of association. This is reflected between 110 K and 260 K in the growth of the broad bands at about 1600 cm\(^{-1}\) in the infrared spectra, assignable to chelated carbonyl bonds (Fig. 3B), and in the shift of the ultraviolet absorption to 310 nm.

The onset of nucleation and spontaneous crystallization above 260 K does not appear to be time dependent, as a sample exhibiting a spectrum as shown in Fig. 3B remained unchanged when left for over 60 h at that temperature. Likewise, film deposition at 170 K resulted in an IR spectrum with a peak pattern nearly identical to one obtained by heating a film from 10 to 170 K, pointing to a strict temperature control of the degree and type of associations present in these films.

Such a temperature dependence is similar to that found in solids undergoing a phase transition and suggests the existence, or spontaneous formation, of interdependent, glass-like structures in these aggregates. The exact nature of associations present cannot be derived from the ultraviolet and infrared spectra, but the simultaneous presence of both ‘free’ and chelated carbonyl frequencies in the IR spectra suggests the gradual development of the herring bone molecular arrangements as found in the crystalline form above 260 K (in which still a significant amount of more or less associated carbonyl groups continue to persist). The sudden transition observed above 260 K, with the formation of doublets of both the associated and chelated carbonyl frequencies (at 1781/1745 and 1635/1546 cm\(^{-1}\), respectively) and without any significant change of their relative intensities, is in agreement with such molecular organization in the intermediate temperature range (100–260 K).

The different behaviour of crystallites formed above 260 K from thin and thick films (cf. Figs. 3 and 4) suggests an interrelation between crystal size and lattice energies. The IR spectra indicate, that crystallites formed from thin films above the transition temperature of 260 K, which can be assumed to be the significantly smaller ones, consist nearly quantitatively of the ‘hot’ modification (cf. insert Fig. 4C). By contrast, the crystallites from the thicker films show the coexistence of both modifications at the same temperature. These transition temperatures
are well below the 348 K normally observed during the heating cycle for crystalline 1b [3a, 4].

It thus seem that, as the crystallite size is reduced, the transition temperature from the 'cold' to the 'hot' modification is lowered, i.e., the lattice forces holding the molecules of 1b in the polymeric form are weakened. Similar lowering of the transition temperature with particle size has been observed for the phase transition of ammonium chloride [7] and for the lowering of the loading transition pressure for the absorption of hydrogen on palladium metal [8]. Theoretical treatments for ionic clusters of alkali halides also predict a lowering of the binding energies with reduction of cluster size [9].

Furthermore, as the crystallite size is reduced, the ratio of surface to intercrystalline molecules increases. The continued presence of significant amounts of 'free' carbonyl groups, as indicated by the bands at about 1765 cm\(^{-1}\) in the films recooled to 12 K (with a higher relative intensity in the spectrum of the thin film) shows, that indeed very small crystals with very large surface area are present, especially in the thin films prepared for UV measurements.

The results are in good agreement with the conclusions reached in our previous DSC and IR studies [4], performed on mixtures of macro- and microcrystalline assemblies, which had shown that in such non-homogeneous samples the transition temperatures are broadened and lowered. They also show that the technique of matrix isolation and thin film deposition can successfully be applied to the study of temperature dependent molecular reorganization of systems which are known to undergo phase transitions.

The results obtained in this way thus give a deeper insight into the modes of transformation of initially randomly arranged molecules through an organized but non-crystalline form to finally the microcrystalline state.

### Experimental Part

Details of the experimental equipment used in our photochemical and spectroscopic low-temperature investigations have been described previously [10, 11]. Essentially a closed-cycle cryostat is employed to cool a NaCl optical window to 10–12 K, the temperature being monitored by a thermocouple at the end of the cooling stage and by a second thermocouple embedded in a drilled cavity close to the window center. The flow of matrix gas is controlled by a calibrated micrometer needle valve and vacuum meter assembly.

The sample, degassed and transferred under argon atmosphere, was deposited from a quartz capillary, temperature stabilized between 243 and 303 K by a Peltier element and between 303 and 473 K by a heater block assembly, with the temperatures being controlled separately via thermocouple readouts. The glass tube was separately outgassed at 473 K before each experiment. When not depositing at 423 K the sample was kept at 243 K. A clear, transparent matrix was obtained even in thin film experiments with a sublimation rate of approx. 3 \(\mu\)g/min·cm\(^2\).

Sublimation rates were established by first depositing onto a small quartz crystal microbalance (TQ-5/100/5 MHz/30 pF; Telequarz GmbH, Neckarbischofsheim) mounted perpendicular to the optical window on the cryogenic window holder [11].

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[5] A sample of 1b rapidly sublimed at high vacuum, and the sublimate deposited onto a coldfinger at 93 K, is initially colourless. However, it slowly turns pale yellow on standing at that temperature. The colour of this solid deepens further as the temperature is allowed to rise to room temperature. The infrared spectrum of this sublimate is identical to that shown in Fig. 3.