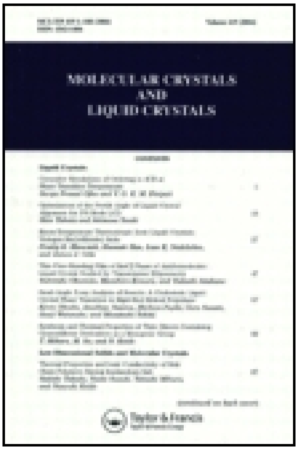

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Crystal Expansion During a Thermochromic Transformation

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CRYSTAL EXPANSION DURING A THERMOCHROMIC TRANSFORMATION

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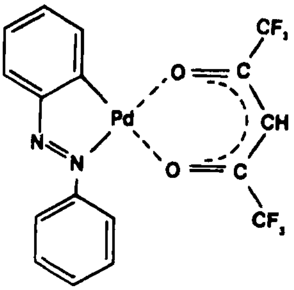
Abstract Phenylazophenylpalladium hexafluoroacetylacetonate can be grown from solution in a yellow or red polymorphic form. The yellow form undergoes a thermal polymorphic transformation to the red form which is accompanied by a sudden discontinuous crystal expansion of 10% of the length of the crystal. The packing patterns of the two crystal forms, as determined by crystal structure analysis, show that the expansion may result from a slip mechanism similar to a Martensitic transformation. The color change is probably due to the rotation of the exocyclic phenyl ring into the plane of the phenylazo group. It remains a puzzle why the expansion is so abrupt and why the color change takes place after the expansion in an independent process.

Phenylazophenylpalladium hexafluoracetylacetonate, I, prepared by cyclometallation of azobenzene[1], can be grown as crystals from hexane at <30°C to give triclinic yellow needles, Ia, or from hot xylene to give triclinic red needles, Ib.



The unit cell of Ia contains two crystallographically independent molecules while that of Ib has only one molecule per asymmetric unit[2], shown in Fig. 1. The intramolecular geometry of the three independent molecules is very similar with the exception of the torsion angle of the exocylic phenyl ring. In Ia this ring is twisted 46.5° and 46.2°, while in Ib the angle is only 14.5°. The decrease in torsion angle would provide for greater intramolecular overlap between the pi-orbitals in this ring and the $C_6H_4N_2$ moiety in which case, a shift of the long wavelength band in the optical spectrum would be expected. Experimentally, such a shift is observed, from 420 to 490 nm.

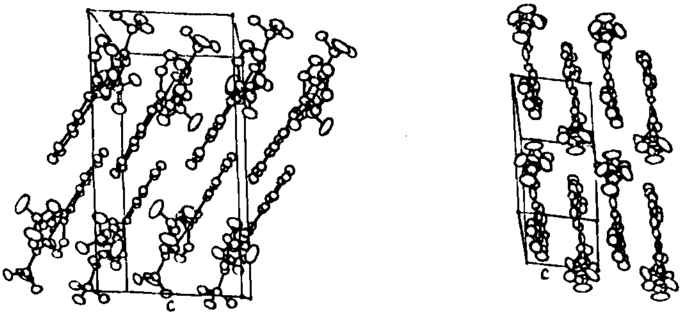


FIGURE 1. Crystal packing patterns of Ia viewed along [100] (left) and lb viewed along [010].

In Ia inversion related molecular stacks parallel to c, the long needle axis, contain alternating Pd-Pd contacts of 3.8 and 4.8Å, which seem too long for metal-metal bonding. In Ib there are also molecular stacks parallel to the needle axis, but in this case the molecules within the stack are inversion related, the Pd-Pd contacts are shortened to 3.5Å and they form a zigzag chain along the c-axis.

When crystals of Ia are heated to 90±10°C they undergo a sudden discontinuous expansion of about 10% along the needle axis with no measurable change in width. If the crystals are heated on only one face, sufficient mechanical strain develops that they jump off the hot stage. On further heating a red phase front develops which moves along the needle axis until the entire crystal is an opaque red color. At this point a powder pattern of the red material indicates that it is polycrystalline and that it is the same crystal form as Ib grown from solution. ΔH for both the expansion and color change as measured by differential scanning calorimetry is 2.1 kcal/mole. The solid state rearrangement is irreversible but through dissolution, the two crystal forms are interconvertible.

A slip mechanism consistent with the packing patterns of the two polymorphs and with the observed crystal expansion along the needle axis involves interleaving of the two i-related molecular stacks in Ia, shown schematically below.

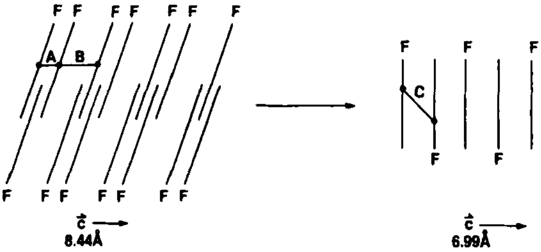


FIGURE 2. A schematic view of the two packing patterns of Ia (left) and Ib, showing the Pd-Pd contacts as A (3.8Å), B (4.8Å), and C (3.5Å). The hexafluoroacetylacetonate groups are indicated by an F in order to show molecular orientation.

This would lead to i-related molecules within each stack, as observed in the structure of Ib. However, if the mechanism were this simple then the yellow crystals should turn red at the same time that they undergo expansion. We have tried to identify an intermediate phase which has resulted from the expansion, prior to color change. Samples can be isolated at this point, but spectroscopic analyses and diffraction patterns show only that the sample is still crystalline and consists of highly mosaic domains of Ia. There is no evidence for any other crystalline phase.

Understanding of the correlation of molecular structure, crystal packing modes, and solid state chemical and physical properties of organic solids is still primitive compared to our understanding of organic reactions and rearrangements in solution. Clearly more work is needed in order to understand the molecular basis for the solid state rearrangements described here. Hopefully in the near future techniques such as solid state NMR and phonon spectroscopy will become readily available in order to study the dynamics of transformations in the organic (and organometallic) solid state.

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