Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

An X-Ray Diffraction Study of the Substructure-Superstructure Transformation in α-Bis(1,2-Benzoquinonedioximato)palladium(II), α-Pd(bqd)$_2$

T. J. Kistenmacher [a] [b], R. Destro [a] [c], R. E. Marsh [a] & S. Samson [a]

[a] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, 91125, U.S.A.

[b] Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland, 21218

[c] Istituto di Chimica Fisica e Centro CNR, Via Golgi 19, 20133, Milano, Italy

Version of record first published: 21 Mar 2007.

To cite this article: T. J. Kistenmacher, R. Destro, R. E. Marsh & S. Samson (1980): An X-Ray Diffraction Study of the Substructure-Superstructure Transformation in α-Bis(1,2-Benzoquinonedioximato)palladium(II), α-Pd(bqd)$_2$, Molecular Crystals and Liquid Crystals, 62:3-4, 173-179

To link to this article: http://dx.doi.org/10.1080/00268948008084020

Mol. Cryst. Liq. Cryst., 1980, Vol. 62, pp. 173–180
0026-8941/80/6204-0173$06.50/0

An X-Ray Diffraction Study of the Substructure-Superstructure Transformation in α-Bis(1,2-Benzoquinonedioximato)palladium(II), α-Pd(bqd)$_2$†

T. J. KISTENMACHER,‡ R. DESTRO,§ R. E. MARSH, and S. SAMSON
Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, U.S.A.

(*Received March 19, 1980*)

X-Ray diffraction studies of the structure of the α-form of bis(1,2-benzoquinonedioximato)-palladium(II), α-Pd(bqd)$_2$, at four different temperatures are reported. At 108 K a mainly second-order phase transformation from a centrosymmetric subcell structure (space group Ibam, with cell vectors a, b, and c) to a polar, commensurate supercell structure (Pcc2, with $a' = a$, $b' = 4b$, $c' = c$) takes place. The superstructure results from both translation and rotation of the molecules. It can be described in terms of a transverse modulation wave extending perpendicular to the stacking direction resulting in an undulation of the stacks with a maximum displacement of 0.84 Å at 19.5 K. There is no evidence of dimerization within the stacks.

INTRODUCTION

Structural phase transitions in quasi one-dimensional inorganic (e.g., the cyano complex KCP) and organic (e.g., those containing TTF or TCNQ) materials have been the subject of numerous investigations by X-ray diffraction and by elastic and inelastic neutron scattering.[1] Recently, a new

---

† Contribution No. 6165 from the Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology. Support of this research through the following granting agencies is gratefully acknowledged: (a) National Science Foundation [Grant No. DMR-74-19029A1 (S. S.) and Grant No. DMR-78-23957 (T. J. K.)]; (b) Fullbright-Hays Fellowship (R. D.); (c) NIH Grant No. GM 16966 (R. E. M.).

‡ Permanent address: Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.

§ Permanent address: Istituto di Chimica Fisica e Centro CNR, Via Golgi 19, 20133 Milano, Italy.

system of compounds with quasi one-dimensional structural and electrical properties, the bis(1,2-dionedioximato) complexes with Ni, Pd, and Pt, has attracted considerable attention.[2] A particularly interesting example is $Pd(bqd)_2$, where bqd is the ligand 1,2-benzoquinonedioximate, Figure 1.

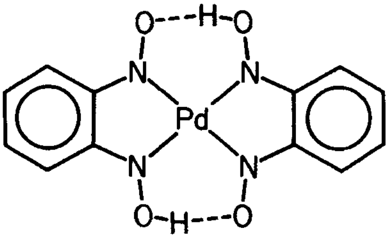

FIGURE 1 A schematic diagram of bis(1,2-benzoquinonedioximato)palladium(II), $Pd(bqd)_2$.

Upon addition of a halogen such as I_2, this compound undergoes partial oxidization to form a charge-transfer complex.[2,3] The unhalogenated compound crystallizes in two different modifications: the α-form (orthorhombic) in which the flat molecules are stacked on top of one another with their planes rigorously perpendicular to the stacking direction,[4] and the β-form (monoclinic)[5] in which the normals of the molecular planes are inclined by about 25° to the stacking direction. Brill *et al.*[6] found striking optical anisotropies, characteristic of one-dimensional electronic effects, in crystals of the α modification but relatively isotropic effects in the β modification. The same authors also observed a very large change in Young's modulus and in the internal friction for α-$Pd(bqd)_2$ at about 100 K, which suggested a phase transition involving the displacements of the molecules. In addition, they observed distinct changes in the powder X-ray diffraction pattern when the sample was cooled with liquid nitrogen. Most striking was an apparent splitting of a peak corresponding to a d-spacing of about 3 Å, suggesting a dimerization along the stacking direction which would lead to two sets of non-equivalent Pd-Pd distances. The nature of the driving force for this kind of distortion had to be left open to question, since the unoxidized compound is a filled-band insulator without the inherent ability to form charge-stabilized dimers.

Our detailed crystallographic studies of single crystals of α-$Pd(bqd)_2$ at temperatures down to 19.5 K have now shown that the phase transition does not involve dimerization but rather results in a supercell which can be described in terms of a transverse modulation[7] wave extending perpendicular to the stacking direction.

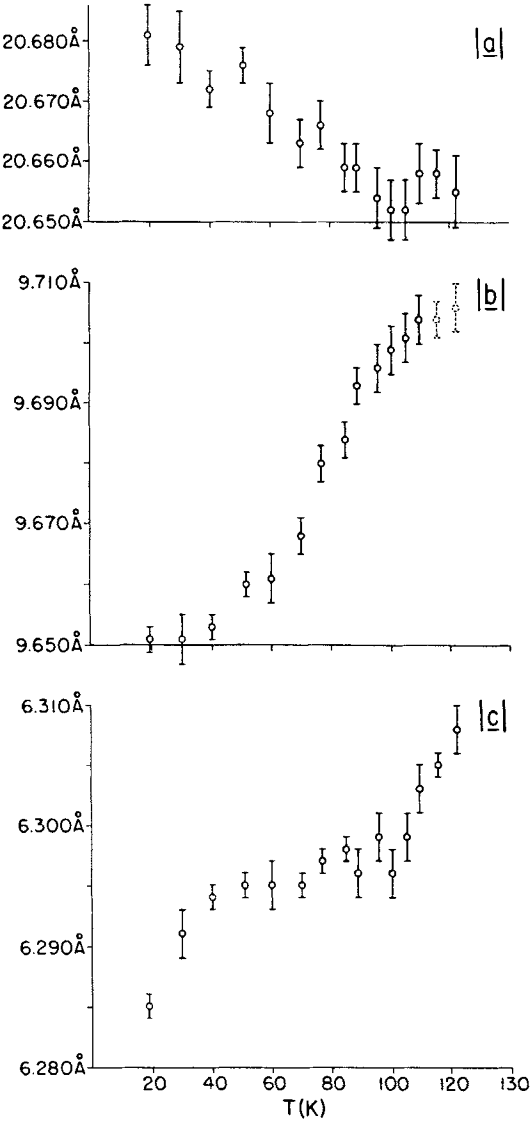

FIGURE 2 Temperature dependence of the unit-cell constants for α-Pd(bqd)$_2$. For $T > T_0$ ($\sim$108 K), the cell constant b is $\sim$9.7 Å (dashed circles); below T_0, b quadruples and superlattice reflections (h, $k/4$, l in the subcell indexing) are observed. Error bars indicate one esd.

EXPERIMENTAL

We have collected complete X-ray diffraction data for a single crystal of α-Pd(bqd)$_2$ at four different temperatures (19.5 K, 76 K, 122 K, and 295 K).[8] The crystals were kindly supplied by Dr. J. W. Brill. A locally designed and built low-temperature diffractometer was used, consisting of a closed-cycle refrigerator, an E & A full-circle and base goniometer, a Syntex P$\bar{1}$ interface (and software package), a graphite monochromator of local design, and a molybdenum-target X-ray tube.[9] The system is capable of maintaining temperatures down to about 18 K for long periods of time at very low cost, so that care was taken to assure that each change in the intensity, position, or shape of a diffraction peak was complete. Thus, we monitored throughout this temperature range the intensities and spacings of a number of selected reflections, having reasonable confidence that the crystal had attained thermal equilibrium at each temperature. We find that the phase transition is accompanied by formation of a supercell in a second-order (or nearly second-order) fashion at about 108 K. The supercell is commensurate with the room-temperature subcell but is primitive and has a volume four times that of the body-centered room-temperature cell ($a' = a, b' = 4b, c' = c$). Changes in lattice constants in the range 20 K–120 K are shown in Figure 2. Strong variations of intensity with temperature are shown by both subcell

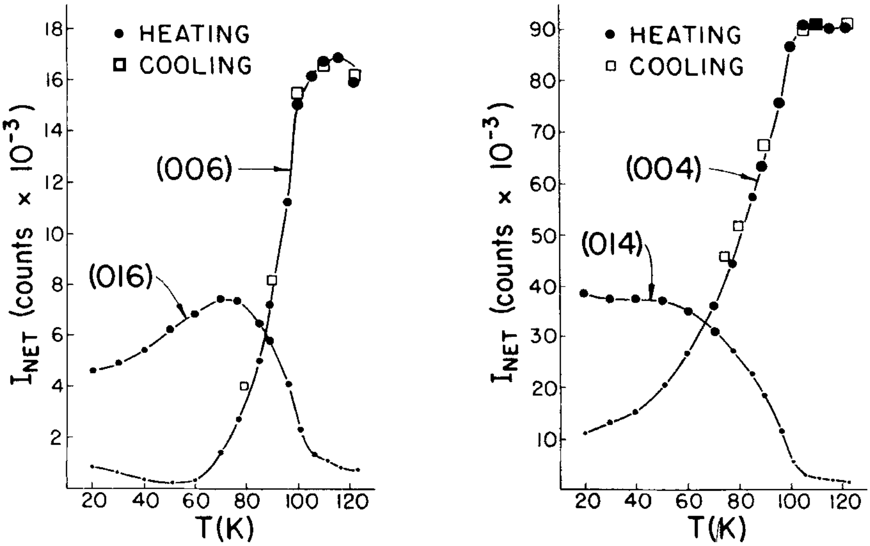

FIGURE 3 Temperature dependence of two sublattice [(006) and (004)] and two superlattice (satellite) [(016) and (014)] intensities. Both heating and cooling data are presented; the relative size of each datum point is bounded at one esd. Solid lines are meant only as a "guide to the eye."

and supercell reflections (Figure 3). Above 108 K, the structure is based on the space group Ibam (D_{2h}^{26}), with $Z = 4$ and 2/m (C_{2h}) symmetry imposed on the molecules. Below 108 K the space group becomes Pcc2 (C_{2v}^{3}) with $Z = 16$. As required for a second-order phase transition, the space group of the superstructure is a subgroup of that of the substructure.

While most of the Bragg reflections corresponding to the low-temperature supercell are relatively weak, enough of them were sufficiently intense to allow us to model the superstructure by conventional crystallographic methods.[10] For this purpose we made use of a detailed knowledge of the subcell structure above the transition (122 K) and of the modulated subcell structure—that is, the "average" structure derived from the subcell reflections alone—below the transition (75 K); we also made extensive use of a Patterson map based on the entire 19.5 K data set.

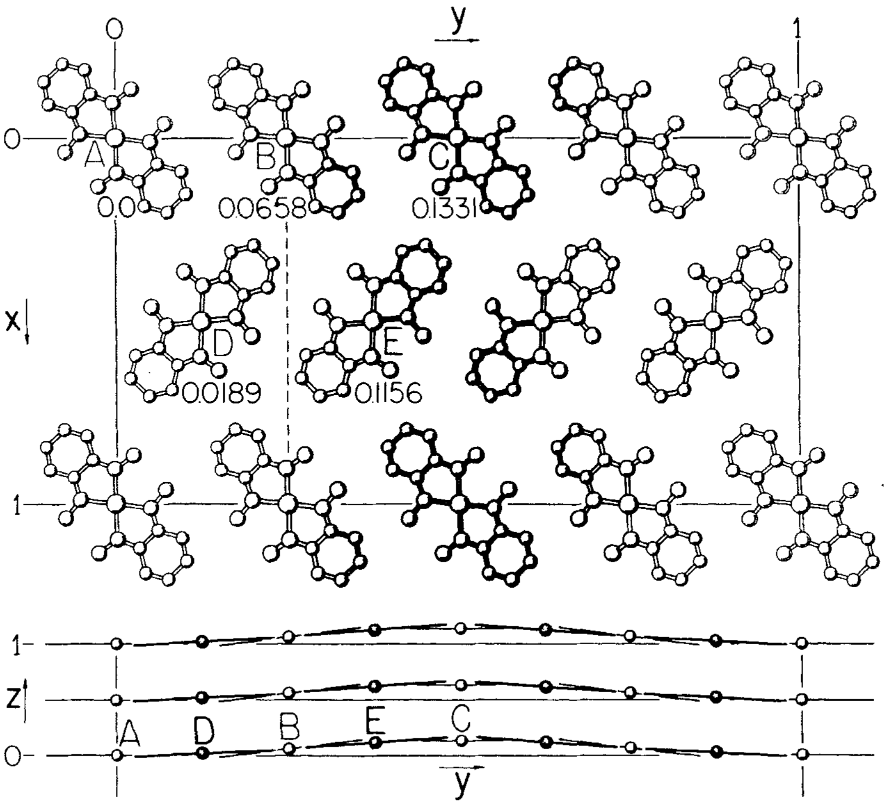

FIGURE 4 The superstructure at 19.5 K. Top: one layer of molecules, viewed along the stacking direction *c*. The relative heights of the five independent molecules are given in units of $|c|(=6.28$ Å); the dashed line demarcates the room-temperature subcell, in which all molecules are at $z = 0.0$. Bottom: A view along *a*, showing the modulation wave along *b*.

DESCRIPTION AND DISCUSSION

The resulting structure in space group Pcc2 is polar and has five symmetrically-independent molecules in the unit cell, of which two (A and C, Figure 4) have crystallographic symmetry 2 (C_2) and the remaining three lie in general positions with no imposed symmetry. The modulation is brought about by displacement of adjacent stacks along the stacking axis *c* and by rotation of the molecules about the *a* and *c* axes ranging up to 7°, while the stacks remain parallel to *c*. The result is an undulation of the molecules that can be described in terms of a transverse wave of period $b' = 4b$ and amplitude 0.42 Å (one-half of the maximum displacement of the stacks) as shown at the bottom of Figure 4. There is no evidence of dimerization along the stacking axis, and the apparent splitting of the 3.0 Å reflection noted by Brill *et al.*[6] actually results from the intensity build-up of supercell reflections from diffraction planes well inclined with respect to the stacking planes.

In contrast to the phenomenon we have observed here for this filled-band insulator, the modulation wave observed in the mixed-valence complex $K_2Pt(CN)_4Br_{0.3}\cdot(3.2)H_2O$(KCP) is longitudinal with an amplitude of only 0.03 Å and extends parallel to the stacking axis,[11] consistent with a charge-density wave instability in the d_z^2 band due to the platinum atoms. In our case the modulation wave is commensurate with the structure while in KCP it is incommensurate.

We hope that our results will inspire further experiments to characterize some macroscopic properties of $Pd(bqd)_2$. For example, the onset of a polar super-structure below ~108 K may well be accompanied by a para-electric-ferroelectric transition.

References

1. (a) R. Comes, M. Lambert, H. Launois, and H. R. Zeller, *Phys. Rev. B* **8**, 571 (1973); (b) R. Comes, M. Lambert, and H. R. Zeller, *Phys. Stat. Sol.*, **58**, 587 (1973); (c) B. Renker, H. Rietschel, L. Pintschovius, W. Glaser, P. Bruesch, D. Kuse, and M. J. Rice, *Phys. Rev. Lett.*, **30**, 1144 (1973); (d) B. Renker, L. Pintschovius, W. Glaser, H. Rietschel, R. Comes, L. Liebert, and W. Drexel, *Phys. Rev. Lett.*, **32**, 836 (1974); (e) J. W. Lynn, M. Iizumi, G. Shirane, S. A. Werner, and R. B. Saillant, *Phys. Rev. B* **12**, 1154 (1975); (f) K. Carneiro, G. Shirane, S. A. Werner, and S. Kaiser, *Phys. Rev. B* **13**, 4258 (1976). See also: R. Comes and G. Shirane, in *Highly Conducting One-Dimensional Solids*, edited by J. T. Devreese, R. P. Evrard and V. E. Van Doren (Plenum Press, New York, 1979).
2. L. D. Brown, D. W. Kalina, M. S. McClure, S. Schultz, S. L. Ruby, J. A. Ibers, C. R. Kannewurf, and T. J. Marks, *J. Amer. Chem. Soc.*, **101**, 2937 (1979).
3. H. Endres, H. J. Keller, M. Megnamisi-Belombe, W. Moroni, and D. Nothe, *Inorg. Nucl. Chem. Lett.*, **10**, 467 (1974).
4. I. Leichert and J. Weiss, *Acta Crystallogr. B* **31**, 2709 (1975).
5. H. Endres, M. Megnamisi-Belombe, W. A. Little, and C. R. Wolfe, *Acta Crystallogr. B* **35**, 169 (1979).
6. J. W. Brill, M. Megnamisi-Belombe, and M. Novotny, *J. Chem. Phys.*, **68**, 585 (1978).

7. Historically, the term "modulated" has been applied to incommensurate superlattice transformations (P. M. deWolff, *Acta Crystallogr. A* **30**, 777, 1974 and *A* **33**, 493 (1977); A. Janner and T. Janssen, *Phys. Rev. B* **15**, 643 (1977)). We use here, however, the broader definition of J. M. Cowley, in *Modulated Structures—1979*, AIP Conference Proceedings, No. 53, p. 3: modulated structure "can be used to describe any periodic, or partially periodic perturbation of a crystal structure with a repetition distance appreciably larger than the basic unit cell dimensions."
8. Details of the X-ray diffraction analyses, including refinements at 295 K, 122 K, 76 K, and 19.5 K, will be published elsewhere: T. J. Kistenmacher and R. Destro, to be published.
9. S. Samson, E. Goldish, and J. Dick, *J. Appl. Cryst.*, (in press).
10. The 19.5 K model was based on rigid α-Pd (bqd)$_2$ molecules with idealized 2/m symmetry and dimensions from our 122 K analysis (Ref. 8). The positions and orientations of the molecules were adjusted using conventional difference-Fourier methods; the final R value ($=\Sigma||F_0| - |F_c||/\Sigma F_0$) was 0.15 for the 1973 reflections with positive net intensity, out of a total of 2625 measured reflections.
11. C. F. Eagen, S. A. Werner, and R. B. Saillant, *Phys. Rev. B* **12**, 2036 (1976).